CHEMISTRY OF PALLADIUM AND PLATINUM ARYLAZOOXIMATES

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in Partial Fulfilment of the Requirements
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DOCTOR OF PHILOSOPHY

By
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to the
DEPARTMENT OF CHEMISTRY
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STATEMENT

I hereby declare that the matter embodied in this
thesis is the result of investigations carried out by me
in the Department of Chemistry, Indian Institute of Technolog
Kanpur and in the Department of Inorganic Chemistry, Indian
Association for the Cultivation of Science, Calcutta (under
permission from IIT Kanpur) under the supervision of Professo
A. Chakravorty.

In keeping with the general practice of reporting
scientific observations, due acknowledgement has been made
wherever the work described is based on the findings of other
investigators.

Pradip Kumar Mascharak

Kanpur:
January 1979.

CERTIFICATE I

Certified that the work 'CHEMISTRY OF PALLADIUM AND PLATINUM ARYLAZOOXIMATES' has been carried out under my supervision and the same has not been submitted elsewhere for a degree.

(A. Chakravorty)
Thesis Supervisor

DEPARTMENT OF CHEMISTRY

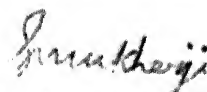## INDIAN INSTITUTE OF TECHNOLOGY, KANPUR, INDIA.

CERTIFICATE II

This is to certify that Mr. Pradip Kumar Mascharak h satisfactorily completed all the course requirements for the Ph.D. degree programme in Chemistry. The courses include:

Chem 501   Advance Organic Chemistry

Chem 521   Chemical Binding

Chem 523   Chemical Thermodynamics

Chem 524   Modern Physical Methods in Chemistry

Chem 534   Electronics for Chemists

Chem 541   Advance Inorganic Chemistry I

Chem 542   Advance Inorganic Chemistry II

Chem 626   Solid State Chemistry

Chem 800   General Seminar

Chem 801   Graduate Seminar

Chem 900   Graduate Research

Mr. Pradip Kumar Mascharak was admitted to the candid of the Ph.D. programme in January 1977 after he successfully completed the written and oral qualifying examinations.

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PREFACE

This thesis originated from our attempt to develop chemistry of arylazooximates of palladium and platinum. Spe[c]-scopic techniques have been largely used to explore the str[u]-ctural patterns of the different species obtained from vari[ous] interesting reactions. Part of the investigation has been ca[rried] out in the Department of Inorganic Chemistry, Indian Associ[ation] for the Cultivation of Science, Calcutta.

The thesis deals primarily with palladium chemistry[;] some aspects of the chemistry of platinum constitute a secon[d] feature. It consists of six chapters of which five are dev[oted] to palladium and one to platinum. In Chapter I, some aspect[s] of the known chemistry of palladium in various oxidation sta[tes] are briefly reviewed. The synthetic methods and structural features of the halo-bridged and bis- arylazooximates of palladium are described in Chapter II. Chapter III and IV concern the bridge-splitting and ring-opening reactions of t[he] halo-bridged arylazooximates of palladium. The ring-opening oxidative reactions of the bis-arylazooximates of palladium constitute the subject matter of Chapter V. The last Chapte[r] (Chapter VI) contains the results of preliminary investigati[on] on the chemistry of the arylazooximates of platinum.

A considerable volume of literature has been cited throughout the thesis. The author accepts the responsibilit[y] for purely unintentional oversights and errors that have, no doubt, crept in.

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CHAPTER I

INTRODUCTION

Abstract: In this Chapter some aspects of the known chemistry of palladium are reviewed in brief outline. The objective of the work reported in this thesis is presented in this background.

I.1 GENERAL CONSIDERATION

This thesis mainly deals with some synthetic and structural aspects of a group of palladium(II) complexes. The corresponding platinum(II) systems get a minor place. For palladium, all oxidation states in the range 0 to +4 are known. The most common oxidation state is +2. The +3 oxidation state is rare and will not be considered any further. Before we delineate the objective of our work, some gross features of the chemistry of palladium in the oxidation states 0, +1, +2 and +4 will be summarised in bare outline. The known chemistry of palladium and platinum is very extensive. Comprehensive coverage of some aspects may be found in several recent books[1,2,3].

I.2 CHEMISTRY OF PALLADIUM: AN OUTLINE

I.2.A Zero Oxidation State

In the zero oxidation state, palladium forms a range of complexes. These complexes are generally prepared by reducing the divalent compounds with suitable reducing agents like hydrazine or KBH_4. The zerovalent complexes usually have coordination numbers in the range 2 to 4. The stabilisation of zerovalent palladium complexes generally needs ligands which are both strong σ-donors and π-acceptors. Some of the ligands are phosphines[4,5] arsines[4,5], phosphites[4], isocyanides[6,7], cyanide[8], acetylide[9] and nitric oxide[10]. A few

of these systems will be discussed in the following paragraphs.
The zerovalent compounds of the nickel triad follow the stabi-
lity order $Ni > Pt > Pd$.This is paralleled by the trend in
the function (EA-IP) where EA refers to the electron affinity
and IP the ionisation potential of the metal in its d^{10}
valence state[11]. The σ-bond strength is related to the trend
in EA, $Pt > Pd \approx Ni$. The π-back bonding strength varies with
-IP and is $Ni > Pt \approx Pd$. In effect, Ni is a strong π-bonder,
Pt is a strong σ-bonder, but Pd is relatively weak in both.

a. Phosphines

The phosphine chemistry of zerovalent palladium (and
platinum) is extensive. The triphenylphosphine complexes
$\left[M(PPh_3)_4 \right]$ where M = Pd or Pt, are obtained by borohydride
reduction of an aqueous alcoholic solution of excess phosphine
and K_2PdCl_4 or K_2PtCl_4[12]. Powdered $Pd(NO_3)_2$ reacts with
excess triphenylphosphine (the phosphine itself acts as the
reducing agent) in benzene[4] to give $\left[Pd(PPh_3)_4 \right]$. Zerovalent
palladium and platinum complexes with chelating phosphines and
arsines have been reported by Chatt[13]. The electrochemical
reduction of the corresponding bivalent metal complexes with
the chelating phosphine $Ph_2PCH_2CH_2PPh_2$ to the zerovalent ones
(and also the intermediate univalent complex for nickel) in
acetonitrile has been investigated by Martelli et al.[14].
By controlled potential electrolysis, the two-electron reduction
products can be isolated in good yields. The cyclic voltammetric

data suggest the increasing ease of reduction in the order Pt, Pd, Ni. The preparation and reactions of zerovalent palladium complex with one fully alkylated phosphine PEt_3 have been described[15,16].

The triphenylphosphine and other tertiary phosphine complexes dissociate in solution to give coordinatively unsaturated species (M = Pd, Pt):

$$\left[M(PPh_3)_4\right] \rightleftharpoons \left[M(PPh_3)_3\right] \rightleftharpoons \left[M(PPh_3)_2\right] \rightleftharpoons \left[M(PPh_3)\right]_n$$
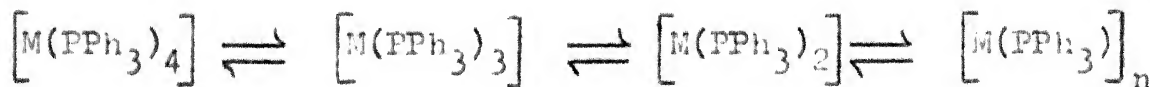
In the case of the palladium(0) complex, this dissociation has been inferred from the very low molecular weights found in benzene solution[4] and in the isolation of species like $\left[Pd(PPh_3)_2\right]$[17] which in solution goes over to $\left[Pd(PPh_3)_4\right]$ and palladium metal. With bulky phosphines, only the Pd(phosphine) species could be isolated even in presence of excess phosphines. Stable two-coordinate palladium(0) complexes with bulky phosphines like $P(Bu^t)_3$, $PPh(Bu^t)_2$ and $P(Cy)_3$ have been reported[18]. These complexes are stable in solution and x-ray studies have revealed nonbonding contacts ($2.7 \sim 2.8^{\circ}A$) of ligand hydrogen atoms to the metal which apparently prevent approach of solvent molecules[18]. However, these complexes show high reactivity towards small molecules like H_2, CO, HX etc to yield $\left[PdH(X)L_2\right]$ type of complexes[19]. The [31]P & [13]C nmr spectra of these 14-electron two-coordinate palladium(0) complexes have been studied[20]. Tertiary phosphines being

strong σ-donors but poor π-acceptors, build up negative charge on the metal which can be dissipated more effectively by π-back acceptance in the trigonal and linear complexes than in a tetrahedral complex and this could be a possible reason of the stability of the coordinatively unsaturated species.

Unlike the platinum(O) complexes which yield hydrido species, palladium(O) complexes, when treated with acids, yield the dihalo complexes like $\left[(PPh_3)_2Pd^{II}X_2\right]$. This is because of the fact that palladium(II)-hydride complexes are unstable both thermally and to excess acid. These reactions come under the general heading of "oxidative addition to zero-valent complexes". Thus $\left[Pd(PPh_3)_4\right]$ reacts with alkali halides, acetylchloride and iodobenzene[21] and because of the ease of cis-trans-isomerisation of palladium(II) complexes, the products are always the trans-palladium(II) isomer $\left[(PPh_3)_2Pd(R)X\right]$. Recently, the mechanism of the oxidative addition of alkyl and benzyl halides to zerovalent palladium complexes has been thoroughly investigated by Stille[22].

The palladium(O) complexes (and those of zerovalent platinum) react with oxygen to give addition compounds[23]. The palladium(O)-oxygen complex $\left[(PPh_3)_2PdO_2\right]$ is unstable above 20°C (the corresponding platinum(O) compound is stable upto 120°C) decomposing to the free metal and triphenylphosphine oxide:

$$\left[(PPh_3)_2PdO_2\right] \longrightarrow Pd + 2\ Ph_3PO$$

Sulfur dioxide reacts with $\left[Pd(PPh_3)_4\right]$ to yield $\left[(PPh_3)_3Pd(SO_2)\right]$[24]. The complexes $\left[(PPh_3)_2MO_2\right]$ (M = Pd, Pt) react with small molecules like sulfur dioxide, nitrogen dioxide and nitric oxide to give the corresponding sulphato, dinitrato and dinitro complexes[25]. In fact, the oxygen molecule in $\left[(PPh_3)_2MO_2\right]$ (M = Pd, Pt) is very reactive and use of these compounds in catalysing the oxidation of triphenyl-phosphine and cyclohexene to triphenylphosphine oxide[26] and cyclohexene-3-one as well as cyclohexene oxide[27] has been suggested.

b. Isocyanides and Cyanide

Palladium(O) isocyanide complexes $\left[Pd(CNR)_2\right]$ are prepared by reducing the palladium(II) isocyanide complexes with isocyanides in presence of a strong alkali[28]. Triaryl-phosphines replace the isocyanide ligands from $\left[Pd(CNR)_2\right]$ to give new zerovalent complexes[28] and treatment of an alcoholic suspension of $\left[Pd(CNR)_2\right]$ with iodine leads to $\left[Pd^{II}I_2(CNR)_2\right]$[4]. The compound $\left[Pd(CNBu^t)_2\right]$ absorbs oxygen to give $\left[Pd(CNBu^t)_2O_2\right]$ which has an infrared spectrum consistent with the presence of a π-bonded oxygen ligand[29]. A zerovalent cyanide complex of palladium $K_4\left[Pd(CN)_4\right]$ has been prepared by treating $K_2\left[Pd(CN)_4\right]$ with potassium liquid ammonia[8].

c. Nitric Oxide

Nitric oxide complexes such as $\left[Pd(NO)_2Cl_2\right]$, $\left[Pd(NO)Cl\right]_n$ and $\left[Pd(NO)_2SO_4\right]$ have been synthesized by passing nitric oxide into palladium(II) chloride or sulphate solutions in either methanol (monomeric products) or water (polymeric products)[30]. The zerovalent metal was identified in each of these complexes by the observed diamagnetism and the N-O stretching frequency around 1800 cm^{-1} in infrared spectrum which is typical of coordinated NO^+.

d. Dibenzylideneacetone

The palladium(O) dibenzylideneacetone complexes are recent additions to the organometallic chemistry of zerovalent palladium. The first dibenzylideneacetone (DBA) complex of palladium(O) $\left[Pd(PhCH = CHCOCH = CHPh)_2\right]$ was obtained by treating a hot methanolic solution of Na_2PdCl_4 containing excess ligand with sodium acetate[31]. Prolong room temperature stirring of a suspension of DBA in aqueous-ethanolic solution of Na_2PdCl_4 yielded the tris complex $\left[Pd(DBA)_3\right]$[32]. The corresponding platinum complexes $\left[Pt(DBA)_2\right]$ and $\left[Pt(DBA)_3\right]$ have also been reported[33]. The nmr and ir data for these DBA complexes[33] indicate that the metal atoms are bound to the carbonyl groups rather than to the double bonds as originally proposed[31]. Recrystallisation of $\left[Pd(DBA)_2\right]$ from chloroform, benzene and methylene chloride yields compounds

of the type $Pd_2(DBA)_3S$ where S = chloroform, benzene or
methylene chloride. The crystal and molecular structures of
the $Pd_2(DBA)_3$ unit in these solvates, however, confirm coordina-
tion through double bonds[34a,b]. In both the chloroform and
benzene solvates, the $Pd_2(DBA)_3$ unit contains three S-_cis_,
trans DBA ligands (structure I) bridging the two metal atoms
coordinated through their olefin groups. In the methylene
chloride solvate, however, two of the DBA ligands are in S-_cis_,
trans configuration while the third is in the S-_cis_,_cis_ form
(structure II). The Pd atoms are all trigonally coordinated.
The complex $\left[Pd(DBA)_3\right]$ has been shown to have a trigonal
coordination geometry about the metal with each DBA bonded to
the metal through one olefin group and each ligand in the
S-_cis_, _trans_ configuration (structure III). The complex
$\left[Pd(DBA)_2\right]$ is believed to be DBA solvate of $Pd_2(DBA)_3$[34a].
Addition of DBA to $Pd_2(DBA)_3$ however, leads to the formation
of $\left[Pd(DBA)_3\right]$[35].

The DBA complexes are all air stable and $\left[Pd(DBA)_2\right]$ is
an useful precursor to other Pd(0) complexes. Various
substitution and addition reactions of the DBA complexes along
with an investigation on the potential utility of these
complexes as homogeneous catalysts have been reported[32,34a,36].

I.2.B +1 Oxidation State

Palladium and platinum in the +1 oxidation state are
relatively rare. Univalent palladium forms an interesting
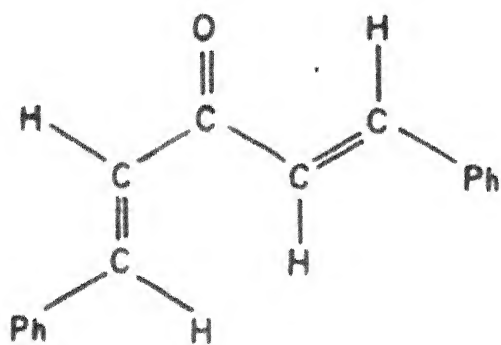
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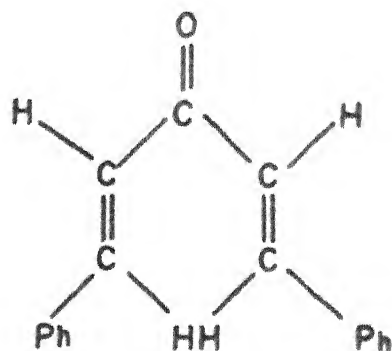
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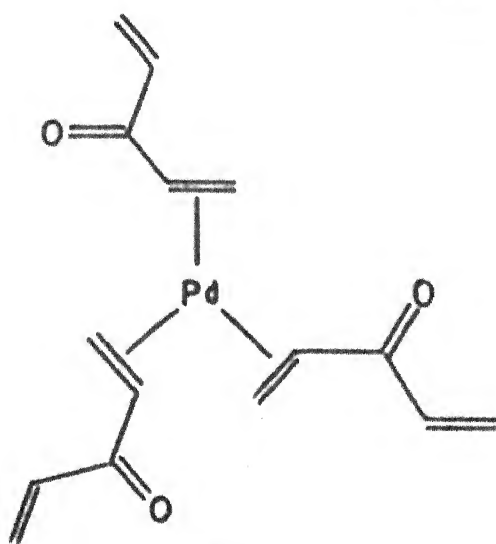
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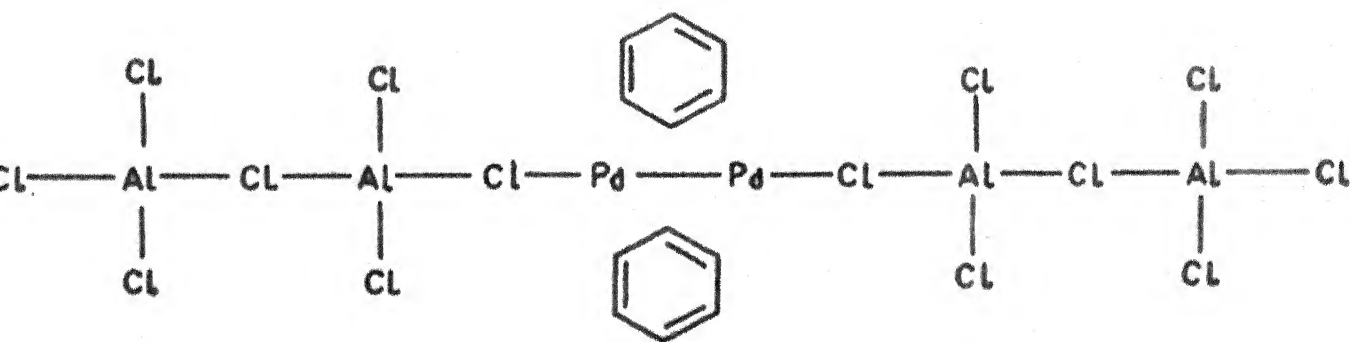
IV

group of compounds containing Pd_2^{2+} unit linked to ligands in various ways. The first reported compound $\left[PdAl_2Cl_7(C_6H_6)\right]_2$, was synthesized by treating $PdCl_2$ in benzene with aluminium and aluminium trichloride. This compound has been well-characterised by x-ray diffraction[37]. It has a quite unusual structure in which a dimeric Pd_2^{2+} unit is sandwiched between two benzene rings (structure IV). The compound is diamagnetic and deposits metallic palladium and $PdCl_2$ when dissolved in tetrahydrofuran or ethanol. X-ray diffraction study[38] on the methyl isocyanide complex of univalent palladium $\left[Pd_2(CNCH_3)_6\right](PF_6)_2$[39] confirms the presence of a direct metal-metal bond (Pd-Pd = 2.531 $^\circ$A). The cation consists of two essentially square-planar coordination planes with a dihedral angle of 86.2° between them. Variable temperature nmr studies on $\left[Pd_2(CNCH_3)_6\right](PF_6)_2$ and $\left[Pd_2(CNCH_3)_5PPh_3\right](PF_6)_2$[40] in acetone-$d_6$ have revealed a fluxional behavior (scheme 1). An explosive purple compound $\left[Pd(C_6H_6)(H_2O)(ClO_4)\right]_n$ of unknown structure has been described by Triggs[41]. A few dimeric palladium(I) complexes containing Pd_2^{2+} unit along with small bridging ligands have also been reported. These complexes are all diamagnetic and involve metal-metal interaction. In course of the palladium(II)-catalysed auto-oxidation of cyclohexa-1,4-diene, red needles of the palladium(I) complex $\left[Pd_2(C_6H_8)(OAc)_2 \cdot \frac{1}{2}(HOAc)\right]$ is formed as a by-product[42]. This complex is thermally unstable and presumably has a Pd-Pd bond and bridging acetate groups. On stirring a methanolic solution of Pd(II)-acetate with four
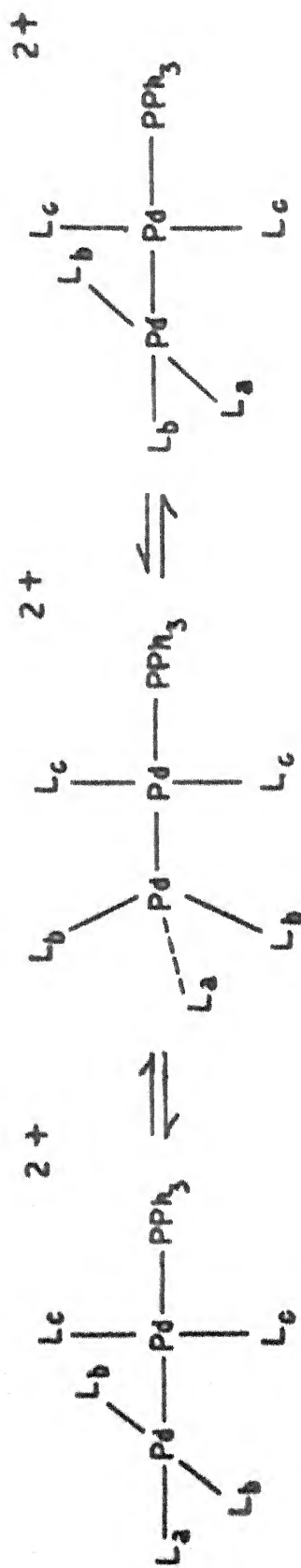
SCHEME 1: FLUXIONAL BEHAVIOR OF $[Pd_2(CNCH_3)_5(PPh_3)]^{2+}$ IN ACETONE – D_6

equivalents of diphenylacetylene at room temperature, the intense green diamagnetic palladium(I) complex $\left[(\mu\text{-PhC} \equiv \text{CPh})(\pi\text{-}C_5Ph_5)_2Pd_2\right]$ (structure V) crystallises out together with some metallic palladium[43]. The diamagnetic carbonylhalide complexes of univalent palladium of the type $(R_4N)_2\left[Pd_2X_2(CO)_2\right]$ where $R = Bu^n$, Pr^n and $X = Cl$, Br, have been reported by Goggin[44]. Detailed infrared and Raman studies have revealed only bridging CO ligands in these complexes. When carbon monoxide is passed through $Pd(PhCN)_2X_2$, where $X = Cl$ or Br, in chloroform, yellow to green polymeric palladium(I) complexes of the type $(PdXCO)_n$, $X = Cl$ or Br, with bridging CO ligands are precipitated[44,45].

Recently some reports on the electrochemical and epr evidence for the existence of paramagnetic Pd(I) and Pt(I) complexes of the maleonitrile dithiolate ligand $S_2C_2(CN)_2^{2-}$ have appeared[46]. However, no such compound has been isolated in pure crystalline form so far.

I.2.C +2 Oxidation State

The +2 oxidation state is the most common for all the elements of the nickel triad. Palladium(II) and platinum(II) are both class 'b' or 'soft' metal ions. For palladium (and also platinum) the usual coordination number is 4 and the usual geometry is square-planar or slight variants thereof[47]. There

is a report that a solution expected to contain bis(N,N'-ethylenedimorpholine)-palladium(II) diiodide is paramagnetic and hence the complex is believed to be tetrahedral[48]. Crystalline PdF_2 has distorted rutile structure and is paramagnetic. It has axially elongated PdF_6 coordination sphere[49]. Diamagnetic $\left[Pd(diars)_2I_2\right]$ has two long axial Pd-I bonds[50]. The five-coordinate complexes of bivalent palladium involve ligands which are good π-acceptors. Some of the square pyramidal complexes have been well-characterised by x-ray diffraction studies[51].

a. Hydrides

The chemistry of the hydride complexes of bivalent palladium and platinum constitutes a rather fresh chapter. The number of hydrido-palladium(II) complexes is, however, limited compared to hydrido-platinum(II) species. Palladium(II)-hydride complexes are unstable thermally and also in both acidic and alkaline media and therefore need highly specific preparative conditions. The stable nickel borohydride complex trans-$\left[(PCy_3)_2NiH(BH_4)\right]$ where Cy = cyclohexyl, reduces trans-$\left[(PR_3)_2PdCl_2\right]$ to yield trans-$\left[(PCy_3)_2PdHCl\right]$[52]. Me_3GeH reacts with trans-$\left[(PEt_3)_2PdCl_2\right]$ under mild conditions forming the rather unstable $\left[(PEt_3)_2PdHCl\right]$[53]. High pressure hydrogenation of trans-$\left[(PEt_3)_2Pd(GePh_3)_2\right]$ leads to trans-$\left[(PEt_3)_2PdH(GePh_3)\right]$. All the known hydride complexes of bivalent palladium are square-planar and have trans-configuration. The hydride ligand

exhibits a strong trans- effect thereby leading to longer Pd-X bonds. The Pd-H stretching frequency usually lies in the range 1900-2250 cm^{-1}. Like all transition metal hydride complexes, the pmr spectra always show very large high-field chemical shifts for the hydride ligand.

b. Complexes with Group VB Donors

The number of palladium(II) complexes with group VB elements is quite large. The occurence of cis-trans-isomerism in square-planar complexes and the mechanism of cis-trans-isomerisation were well- recognised with the platinum(II) complexes of the type ML_2X_2 where L = monodentate nitrogen ligands and X = halogens. Palladium(II) complexes undergo rapid cis-trans-isomerisation and hence until recently only trans-$[Pd(NH_3)_2X_2]$ (X = Cl, Br or I) could be prepared pure. Coe and Lyons[54] have reported the preparation of pure cis-$[Pd(NH_3)_2X_2]$ where X = Cl or Br. However, cis-$[Pd(NH_3)_2(SCN)_2]$ and cis-$[Pd(NH_3)_2(NO_2)_2]$ could not be prepared. The failures indicate that cis-$[Pd(NH_3)_2L_2]$ complexes are only stable with ligands L that lie low in the trans-effect series. The equilibrium thermodynamics and mechanism of cis-trans-isomeri-sation in a number of palladium(II) complexes have been investi-gated by Nelson[55].

Bivalent palladium shows a particular preference for nitrogen donor centers. For example, EDTA normally binds to palladium(II) as a bidentate ligand via the nitrogen atoms[56].

Only at very low concentrations of other coordinating species in solution (including hydroxide ions) EDTA acts either as a tridentate or a tetradentate ligand. In palladium(II) complexes of aromatic heterocyclic ligands such as pyridine, bipyridine and 1,10-phenanthroline which have π-electron systems associated with their aromatic rings, the metal-nitrogen bonds show some properties that are reminiscent of tertiary phosphine ligands. For example, both pyridine[57] and 2,2'-bipyridine[58] can stabilize metal(II)-carbon σ-bonds. The palladium(II) complexes with 8-hydroxyquinoline[59], salicylideneimines[60], glyoxime, dimethyl-glyoxime[61] and other monooximes[62] have all been well-characterised.

Azo complexes of bivalent palladium, trans-$\left[(RN=NR)_2 PdCl_2\right]$ where $R = CH_3$, Ph, substituted phenyl and cyclohexenyl, in which the azo group is bound to the metal atom through a single nitrogen atom, have been prepared by treating $Pd(PhCN)_2Cl_2$ with the azo compound in a nonaqueous solvent like dry benzene[63]. The azo ligand is readily displaced from trans-$\left[(RN=NR)_2 PdCl_2\right]$ by triphenylphosphine, pyridine and 2,2'-bipyridine to give trans-$\left[(PPh_3)_2 PdCl_2\right]$, trans-$\left[(Py)_2 PdCl_2\right]$ and $\left[Pd(bipy)Cl_2\right]$ respectively. The bis azo-palladium complexes have been assigned a trans-structure since they exhibit single palladium-chlorine stretching frequency in their infra-red spectra. The trans-structure of $\left[(PhN=NPh)_2 PdCl_2\right]$ has been confirmed by x-ray diffraction study[64].

Pinkard and his coworkers[65] reported the synthesis of the cis- and trans- isomers of the square-planar glycine chelate of bivalent palladium $\left[Pd(H_2NCH_2COO)_2\right]$. The trans- form is rather unstable and in aqueous solution slow trans- to cis- isomerisation occurs[66] which is unusual in palladium(II) chemistry where trans-isomers are generally stable. The glycine chelate ring is opened at the O-end by perchloric or hydro-chloric acid[66,67]. Glycine and other amino acids[68] usually coordinate through the nitrogen center. However, in the cysteine complexes of Pd(II), the S- and O- atoms of the ligand are coordinated to the metal[69].

The coordination of nucleosides and their constituent bases to palladium has been a subject of recent articles. The nucleoside guanosine is susceptible to attack by palladium salts at the N_7 atom first and subsequent chelation through O_6 and N_7 has been obtained under certain conditions[70]. Such reactions with palladium are much more faster than the corresponding platinum reactions[71]. Adenosine has been shown to bind to diethylenetriamine palladium(II) in aqueous solution either through N_1 or N_7 of the purine base or through both N_1 and N_7 sites simultaneously[72]. Ettorre[73] reported palladium(II)-adenosine complexes of the type $\left[Pd(Adenosine)X_2\right]$ and $\left[Pd(Adenosine)_2X_2\right]$.2DMSO (X = Cl, Br). Interaction of thiamine and its phosphate esters with bivalent palladium (and platinum) gives rise to ionic 1:2 salts in which thiamine is present as a cation and also 1:1 complexes in which thiamine is directly

coordinated to the metal ion[74].

Palladium(II) complexes containing ligands which have phosphorus, arsenic or antimony donor atoms are numerous. An excellent review has already been published[75]. The ER_3 complexes (E = P, As or Sb, R = alkyl or aryl) are generally of two types, namely $\left[(ER_3)_2PdX_2\right]$ and $\left[(ER_3)_2Pd_2X_4\right]$ where X = Cl, Br. The $\left[(ER_3)_2PdX_2\right]$ complexes are formed when solutions of $\left[PdX_4\right]^{2-}$ (X = Cl, Br) or $Pd(PhCN)_2X_2$ (X = Cl, Br) are treated with two equivalents of a tertiary phosphine, arsine or stibine. Pd(II) complexes of para-substituted phenylphosphines $(4-ZC_6H_4)_nP(CH_3)_{3-n}$ (n = 1,2)[76] and 'mixed-ligand' bis-monodentate phosphorus ligand complexes of Pd(II), $\left[LL'PdCl_2\right]$[77] have also been reported. The dimeric halogen-bridged palladium(II) complexes $\left[(ER_3)_2Pd_2X_4\right]$ are synthesised by boiling a mixture of a mononuclear complex $\left[(ER_3)_2PdX_2\right]$ in ethanol or chloroform with Na_2PdX_4 in ethanol[78]. The complexes are all stable, pale yellow to white crystalline solids and in general have trans-configuration[79]. However, tertiary stibine complexes $\left[PdL_2X_2\right]$ (L = Et_3Sb, Ar_3Sb, Cy_3Sb) have trans-configuration for bulky ligands like Cy_3Sb whereas less bulky ligands like Et_3Sb give cis-chlorides and bromides[80]. Complexes of palladium with bulky phosphines like PBu^t_2R often exhibit metallation reactions[81]. A detailed ^{13}C nmr study of several phosphine, arsine and amine complexes of bivalent palladium[82] has indicated that the ^{13}C chemical shift of the carbon atom adjacent to the donor atom and the one in the para position in corresponding

phenyl derivatives can be useful probes for the determination of the complex geometry.

Palladium complexes containing bidentate phosphine ligands have been reviewed by Levason and McAuliffe[83]. Shaw[84] has reported some interesting large ring (12 to 45 membered) complexes of palladium (and platinum) of the type $\underline{trans}$- $\left[\left\{MCl_2\left[Bu_2^tP(CH_2)_nPBu_2^t\right]_x\right\}\right]$ (M = Pd or Pt; n = 8,9,10 or 12; x = 1-3). Several 1:1 and 2:1 complexes of the type $\left[PdCl_2(diars)\right]$ and $\left[PdCl_2(diars)_2\right]$ with different ditertiary arsines are known[85]. The bis-complexes with O-phenylenebis-$\left(dimethylarsine\right)\left[M(PAs)_2\right]^{2+}$ (M = Pd or Pt), on conductometric titration with halide ions, give sharp end-points corresponding to the addition of one equivalent of halide ion[86]. However, although the complexes $\left[PdX_2(PAs)_2\right]$ are conducting in solution, they are six-coordinate (elongated octahedron) in the solid state[50]. Hence, postulate of five-coordinate species on the basis of the titration data is rather ambiguous.

Semi-rigid tetradentate ligands such as QAs and QP (structure VI) form trigonal bipyramidal complexes with bivalent palladium (structure VII)[87]. A less rigid tetra-arsine TAs (structure VIII) forms a square-pyramidal complex $\left[Pd(TAs)Cl\right]^+$ ClO_4^- (structure IX)[88]. Recently one square pyramidal complex of bivalent palladium with monodentate phosphine has been reported[89].
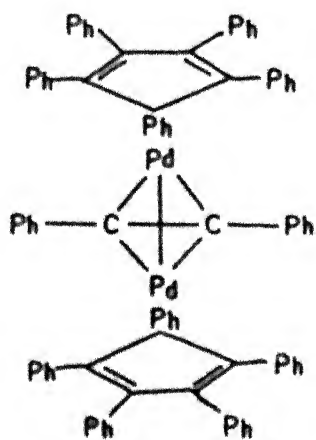
V
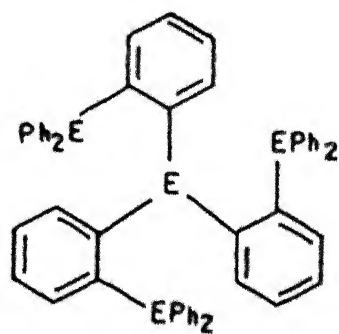
QP(E≡P)
QAS(E≡AS)

VI
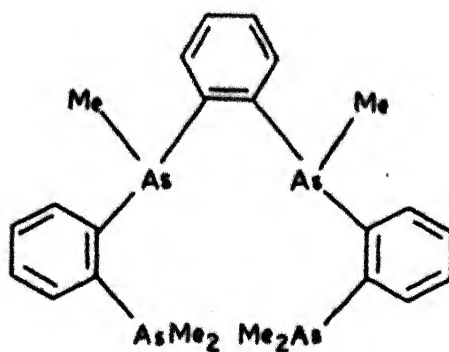
VIII
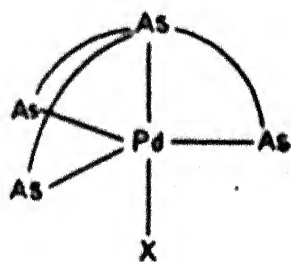
VII
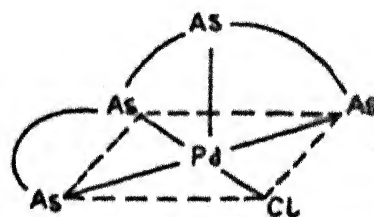
IX

c. Complexes with Group VIB Donors

Since Pd^{2+} is a class 'b' or soft metal ion, it forms stronger complexes with sulfur than with oxygen ligands. Complexes of bivalent palladium with small bidentate oxygen donor anions (sulphate and carbonate) and monodentate oxygen donor anion (nitrate) have already been described[25]. Powell et al [90] have reported the monodentate bicarbonate complexes trans-$\left[PdMe(HOCO_2)L_2\right]$ where L = PEt_3, $PMePh_2$. In the bis-urea complex $\left[Pd(H_2NCONH_2)_2Cl_2\right]$, urea is monodentate and coordinates through the N atom[91]. Similarly in all nitrite complexes of palladium (and platinum also) the metal is bound to the N atom[92]. The crystal structure of palladium(II) acetate, shows that in solid state, it is made up of trimeric units in which each palladium atom is approximately square-planar and joined to the other two palladium atoms by double acetate bridges[93]. Palladium(II) acetylacetonate is prepared by treating $PdCl_2$ with acetylacetone and KOH and recrystallising the product from hot benzene[94]. X-ray diffraction studies have shown that the metal atom and the β-diketone rings are virtually coplanar giving rise to a perfect square-planar geometry about the metal[95]. Acetylacetonates of palladium (and platinum), when treated with Lewis bases like PPh_3 or pyridine, yield products in which the acetylacetone fragment is linked to the metal center through the γ-carbon atom[96]. The γ-carbon bonded species can be readily identified by infra-red and nmr studies.

Similar central-carbon-bonded Pd(II) complexes of ethylaceto-acetate have also been reported[97].

Dialkylsulfides[98] and dialkyl as well as diaryl-selenides[99] form monomeric palladium(II) complexes $\left[Pd(R_2E)_2X_2\right]$ which exist in the _trans_-configuration[100]. Dimethyl- and diethylsulfide also form dimeric complexes $\left[(R_2S)_2Pd_2X_4\right]$ where R = Me or Et, X = Cl or Br. X-ray diffraction studies of $\left[(Et_2S)_2Pt_2Br_4\right]$ and $\left[(Me_2S)_2Pd_2Br_4\right]$ have shown that whereas the palladium(II) compound has the expected bromobridged structure (structure X), the platinum(II) compound has diethyl-sulfide as the bridging ligands[101] (structure XI). On addition of $PdCl_2$ to a concentrated solution of potassium dithiooxalate, the dark colored dithiooxalato complex $K_2\left[Pd(C_2O_2S_2)_2\right]$ crystallises out[102]. The anion is square planar[103] and it coordinates strongly to class 'a' metals via the terminal oxygen atoms[104]. Palladium(II) complexes of thiourea[105], dimethylsulfoxide[106] and dithiobiuret[107] have been reported. The former two ligands coordinate through the sulfur atom giving rise to $\left[PdL_2X_2\right]$ type of complexes whereas the latter yields bis-complex $\left[Pd(dithiobiuret)_2\right]$ in which dithiobiuret acts as a bidentate uninegative ligand coordinating through both the S atoms. The 1,2-dithiolene complexes of palladium and platinum[108] have drawn much attention because of the ease with which they undergo electron-transfer reactions. The electron-transfer reactions of the 1,2-dithiolene complexes of
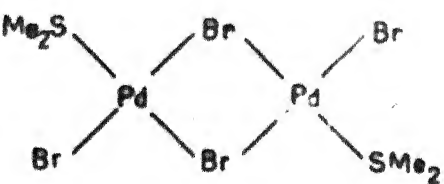
X
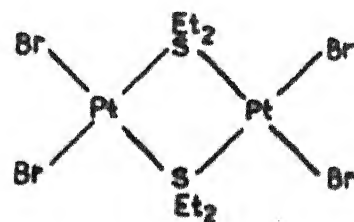
XI
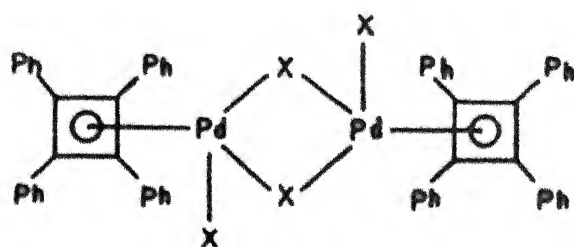
XII
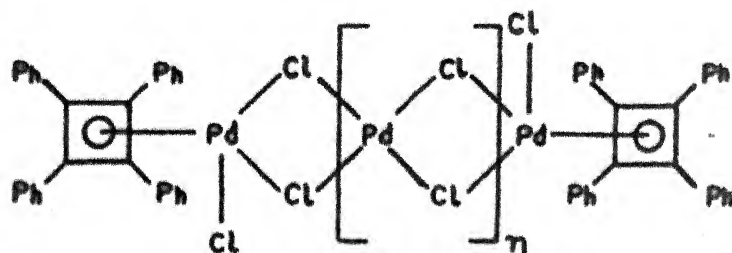
XIII

palladium and platinum have been systematised through a study
of the halfwave potentials of each one-electron step[109].
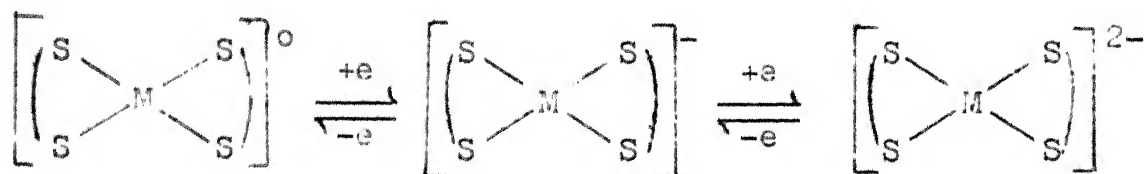
An excellent discussion on the nature of bonding in these 1,2-
dithiolene complexes of the nickel triad can be found in
reference (109).

d. Systems with Metal-Metal Interaction

In some palladium(II) complexes with nitrogen containing
ligands, square-planar units are stacked vertically leading to
metal-metal interaction. These compounds have short metal-metal
distances and exhibit unusual spectroscopic and conductivity
properties[110]. The corresponding platinum complexes viz Magnus'
salts have been studied thoroughly. The few palladium complexes
which are known to exhibit metal-metal interaction are
$[Pd(dimethylglyoxime)_2]$ (Pd-Pd distance 3.26°A)[111]
$[Pd(NH_3)_4][PdCl_4]$ (Pd-Pd distance 3.25°A)[112] and $[Pd(NH_3)_4]$
$[PtCl_4]$ (Pd-Pt distance 3.25°A)[112]. The ionic complexes
$[ML_4]^{2+}[MX_4]^{2-}$ are obtained by treating $[M(NH_3)_4]X_2$ with
$M_2'MX_4$ where M = Pd(or Pt) and M' is an alkali metal. Direct
metal-metal interactions in different forms of dithioacetato
palladium(II) complexes have recently been reported[113].

A few palladium compounds are known where the palladium atom is bound to other transition metals lying in the same square plane. Iron is particularly notable and Pd(II)-iron complexes have been obtained by treating allylpalladium chloride with iron-carbonyl complexes. A stable crystalline palladium(II)-iron complex has been isolated from a mixture of π-allyl-palladium chloride and diphenylphosphine iron tetracarbonyl[114] and its structure has been confirmed by x-ray diffraction study[115].

$$2\left[(PPh_2H)Fe(CO)_4\right] + \left[(\pi-C_3H_5)PdCl\right]_2 \longrightarrow$$

$$\left[\begin{array}{c} Ph_2P \diagdown \diagup Cl \diagdown \diagup Fe(CO)_4 \\ \quad Pd \qquad Pd \\ (CO)_4Fe \diagup \diagdown Cl \diagup \diagdown PPh_2 \end{array}\right] + 2C_3H_6 \quad \ldots\ldots (1)$$
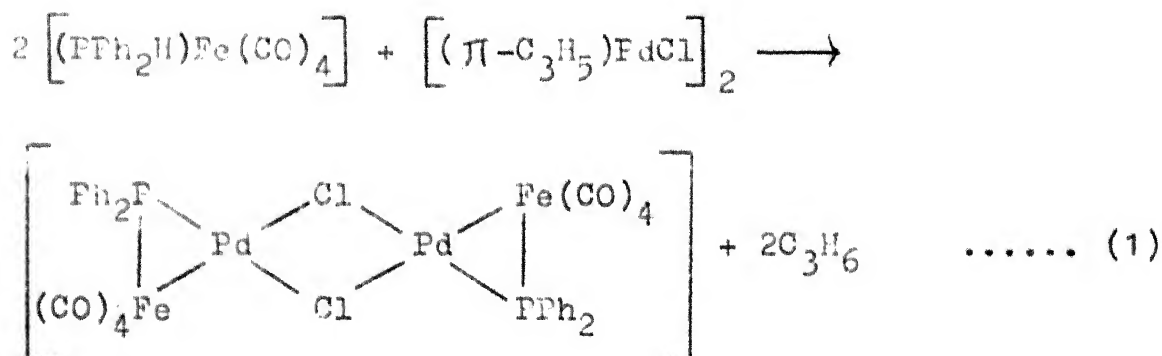
e. Organometallic Chemistry

   (i) <u>Carbonyls, π-Cyclobutadienyl and π-Cyclopentadienyl Complexes</u>:

The palladium carbonyl complexes need special attention since they are implicated in the homogeneous catalysis by palladium salts of the carbonylation of olefins to yield acid chlorides and esters. Apart from the carbonyl species postualted as intermediates in these catalytic reactions, a few carbonyl complexes of palladium have been isolated in free state.

$\left[Pd(CO)Br_2\right]_2$ can be produced by passing carbon monoxide over solid $PdBr_2$ at $180^\circ C$[116]. Treatment of $PdCl_2$ with methanol saturated with carbon monoxide leads to $\left[Pd(CO)Cl_2\right]_n$[117] where n is probably 2. However, if the solution is acidic, the product[118] is the anionic hydrido carbonyl species $\left[PdH(CO)Cl_2\right]^-$. Another carbonyl complex $(NH_4)\left[Pd(CO)Cl_3\right]$ is formed when carbon monoxide is passed through a saturated solution of $(NH_4)_2PdCl_4$[119] in hydrochloric acid. $\left[(PEt_3)_2PdCl_2\right]$, when treated with carbon monoxide in presence of BF_3, yields trans-$\left[(PEt_3)_2Pd(CO)Cl\right](BF_4)$[117].

The reaction product of diphenylacetylene and sodium or ammonium tetrahalopalladate(II) in aqueous ethanol on treatment with anhydrous HX gives π-cyclobutadienyl complexes[120] of the type $\left[(Ar_4C_4)PdX_2\right]_2$ where X = Cl, Br, I (structure XII). However, when diphenylacetylene is allowed to react with $Pd(PhCN)_2Cl_2$ in benzene, the catenated cyclobutadiene-palladium complex XII is formed[121] which on treatment with anhydrous HX yields $\left[(Ar_4C_4)PdCl_2\right]_2$. Transfer of π-cyclobutadiene ligand to other metal is accomplished when $\left[(Ar_4C_4)PdX_2\right]_2$ is treated with metal carbonyls like $Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$ or $Mo(CO)_6$[122]. The π-cyclobutadienyl complexes of palladium have been briefly discussed in a recent review by Efraty[123].

π-Cyclopentadienyl complexes of palladium (and also platinum) are relatively scarce. The general method of their syntheses involves the treatment of the halogen-bridged

palladium(II) complexes with sodium, thallium or mercury
cyclopentadienides[124] viz:

$$\left[(PPh_3)_2Pd_2Br_4\right] + 2\ C_5H_5Tl \xrightarrow[\text{30 min}]{\text{THF, }20^{\circ}C}$$

$$2\left[(\pi-C_5H_5)(PPh_3)PdBr\right] + 2\ TlBr \quad \ldots\ldots \ (2)$$

$$\left[(\pi-C_3H_5)_2Pd_2Cl_2\right] + 2\ C_5H_5Na \xrightarrow{\text{THF/benzene}}$$

$$2\left[(\pi-C_3H_5)Pd(\pi-C_5H_5)\right] + 2\ NaCl \quad \ldots\ldots \ (3)$$
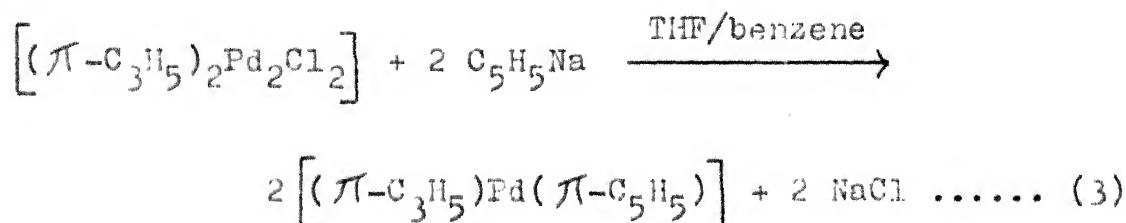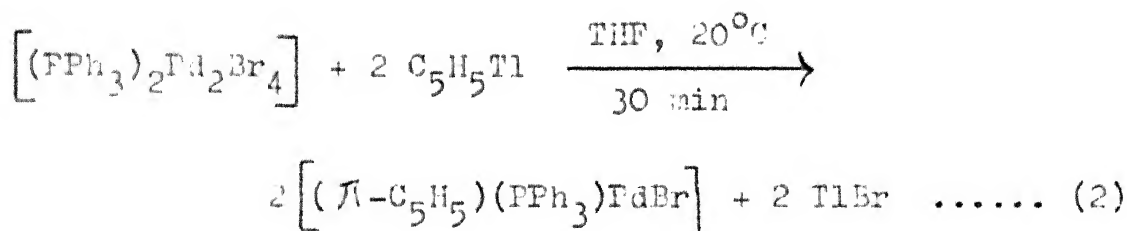
The carbonyl complexes are unstable in air and are
decomposed by moisture. The π-cyclopentadienyl complexes
exhibit a single proton resonance in the nmr spectrum
between 3.71 and 5.40 ppm down field from TMS which is
consistent with symmetrical π-bonding between the cyclo-
pentadienyl ring and the metal[125].

(ii) Complexes Containing Metal-Carbon σ-Bonds:

With the exception of the pentafluorophenyl complex[126],
$\left[(PPh_3)_2Pd^{IV}(C_6F_5)_2Cl_2\right]$, palladium form complexes containing
metal-carbon σ-bonds in +2 oxidation state only.

Treatment of a halometal complex with anionic alkyla-
ting agent such as Grignard or organolithium reagent is the

widely used method for generating Pd(II)-carbon bonds viz,

$$\left[(PEt_3)_2PdBr_2\right] \xrightarrow[CH_3MgBr]{excess} (PEt_3)_2Pd(CH_3)Br$$

$$\xrightarrow{excess\ CH_3Li} \left[(PEt_3)_2Pd(CH_3)_2\right] \quad \ldots\ldots \quad (4)$$
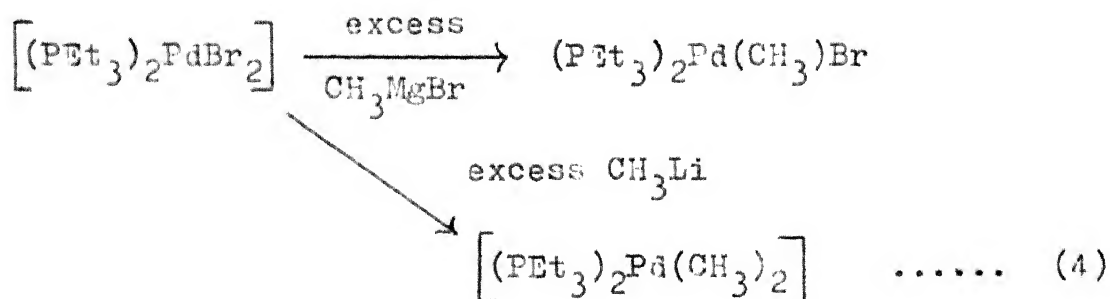
Monoalkyl complexes can be prepared by oxidative addition of alkyl halides to zerovalent complexes of palladium. Reactions in which metal-carbon σ-bonds are formed by insertion into Pd(II)-chlorine bonds are also known[127].

Palladium(II)-alkyl and aryl complexes are somewhat less stable as compared to their Pt(II) analogues. The configuration is usually _trans-_ and the _cis-_ isomers can be prepared only when stabilised by a bidentate phosphine ligand. When heated, the dialkyl complexes appear to undergo homolytic fission with the formation of organic radicals so that when $\left[(PEt_3)_2Pd(CH_3)_2\right]$ is heated at $100^{\circ}C$ in a sealed tube, a mixture of ethane and ethylene is obtained together with a trace of methane[128]. The Pd(II)-carbon stretching frequency lies in the range $455-535$ cm^{-1} which is lower than the range of Pt(II)-carbon stretching frequency $(500-550$ cm$^{-1})$ indicating a higher value for the stretching force constant of the Pd(II)-carbon bond. The limited x-ray diffraction information points to a high _trans-_ influence of the σ-bonded carbon ligands[129].

Pd(II)-carbon σ-bonds are cleaved by water, dilute aqueous acids, hydrogen chloride in benzene, ethanol[128], molecular hydrogen, reducing agents like $LiAlH_4$ or $NaBH_4$[130] and halogens. The alkyl and aryl complexes of palladium(II) are converted to acyl complexes by carbon monoxide[131].

(iii) Orthometallation Reactions:

A class of intramolecular aromatic substitution reactions, commonly referred to as 'Orthometallation reactions' has drawn much attention during the last few years. Some phosphorus and nitrogen ligands, instead of being unidentate as expected are occasionally bidentate with one of the carbon atoms of the ligand acting as the second donor. Many of these complexes involve metallation of a phenyl ring, but a significant number involve the metallation of alkyl groups also. The substitution of an aryl group which is part of a N-donor ligand molecule has been studied extensively with palladium. The simplest example is the reaction between methanolic Li_2PdCl_4 with benzyldialkylamine to give an o-palladiobenzene complex[132]:

$$\ldots\ldots(5)$$
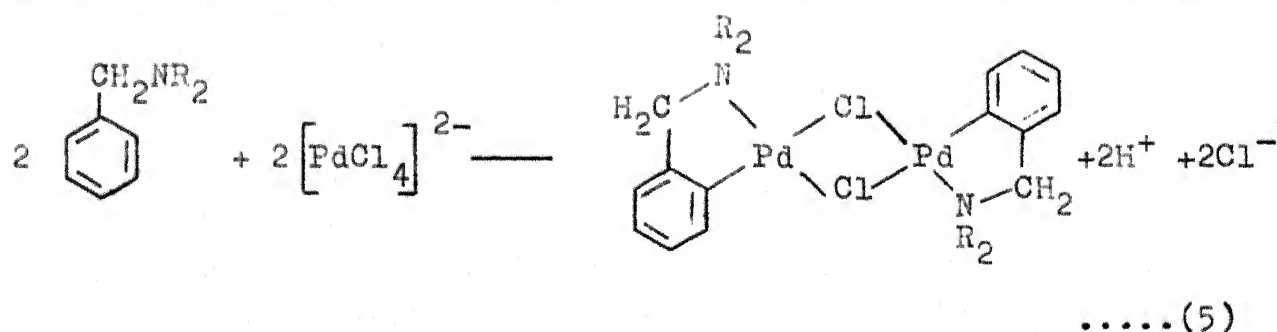
The orthopalladation reaction shows a strong tendency

to form five-membered rings; in the series $C_6H_5(CH_2)_nN(CH_3)_2$, in which n may be O, 1 or 3, only the benzylamine (n = 1) undergoes metallation[132]. Cope and Siekman[130] have reported a classic example in the reaction of azobenzene with MCl_4^{2-} salts where M = Pd or Pt.

$$2 \; \text{[C}_6\text{H}_5\text{N=N-C}_6\text{H}_5\text{]} + 2K_2MCl_4 \xrightarrow[\substack{\text{Room temperature} \\ \text{2 weeks}}]{\text{dioxane/water}} \text{[product]} + 2H^+ + 4KCl + 2Cl^-$$

.......(6)
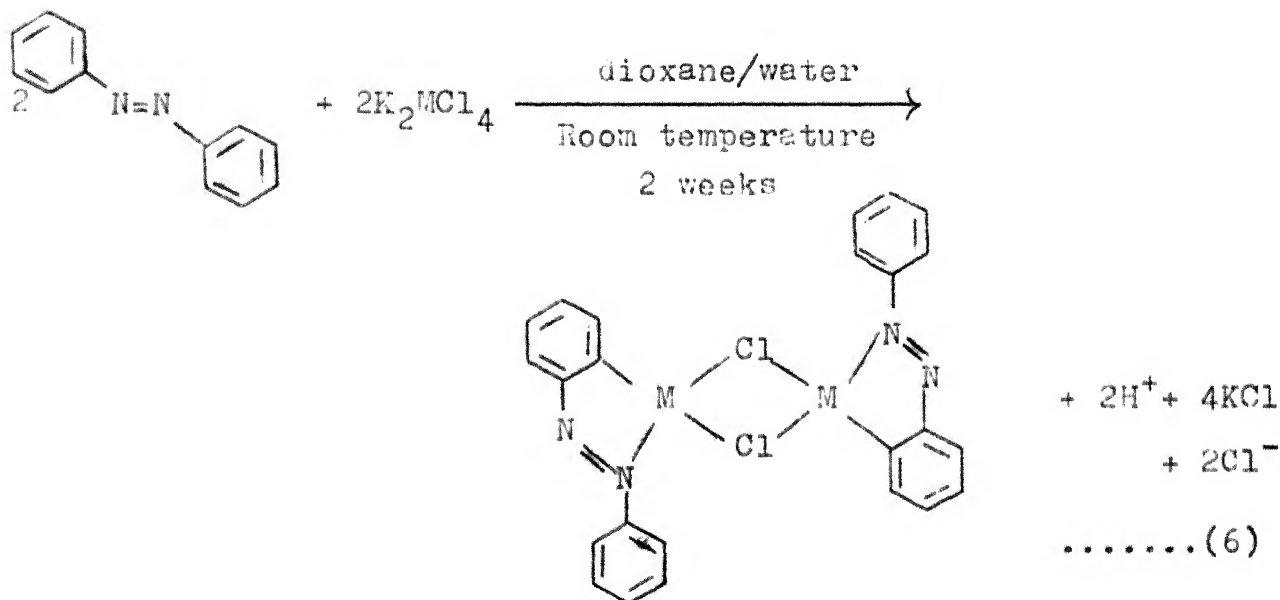
The structure of the product was established by cleaving the metal-carbon σ-bond with $LiAlD_4$ which yielded O-deuterioazobenzene and also by treatment with triethyl-phosphine, which cleaved the Pd-N bond to give trans-$[(PEt_3)_2Pd(C_6H_5N = NC_6H_4)Cl]$ in which palladium is bound to the ortho-carbon atom of one of the phenyl rings[133,129]. When azobenzene bearing a para-substituent on only one of the two aromatic rings are used, the preference for attachment of the metal to the substituted ring falls in the order $OCH_3 > CH_3 > H > Cl$, thus indicating metallation of the more electron-rich ring[134]. The observed substituent effect suggests electrophilic attack

of the aromatic ring by the metal nucleus and a proposed mechanism is described in scheme 2. The first significant interaction between the metal atom and the aromatic ring is the formation of the π-arene complex (step B in scheme 2). The next steps resemble typical aromatic substitution reactions ultimately leading to the dimeric orthometallated product. The nature and detailed mechanism of intramolecular aromatic substitution reactions have been reviewed by Parshall[135]. Orthometallated palladium(II) complexes have been reported with 1-phenylpyrazole[135], N-N-dimethyl-1-naphthylamine[135], 2-phenylpyridine[136,137], Benzo-(h)-quinoline[137], 8-methyl-quinoline[137], 2-phenylquinoline[138], Benzophenoneoxime[139] and with tertiary phosphines[140].

Recently the driving forces for these metallation reactions have been reconsidered. The metallation of N,N'-dialkylbenzylamine and tertiary phosphine ligands arises from two effects. First, the bulky groups bound to N or P atom force one hydrogen atom on one of the groups close to the metal atom for metallation to occur. Thus benzylamine, monoalkylbenzylamine and PMe_2Ph do not give rise to metallated products whereas N,N'-dialkylbenzylamine and PBu_2^tPh yield metallated products readily. Secondly, the bulky groups lower the entropy of rotation of the M-N or M-P bond leading to low entropy of activation for the metallation reaction. Indeed, in **the** compound <u>trans-</u>$\left[(PhN=NPh)_2PdCl_2\right]$ one of the hydrogens on the phenyl rings lie very close to the metal center in the

A

$$[PdCl_4]^{2-} + Ar-N=N-Ar$$

$-Cl^-$ ⇅ $+Cl^-$

$$\left[\begin{array}{c} Cl \\ Cl-Pd-Cl \\ Ar-N=N \end{array}\right]^{-}$$

B

$-Cl^-$ ⇅ $+Cl^-$

Cl
Cl—Pd— ⊕
Ar—N=N

C

Cl
Cl—Pd⁻ H ⊕
Ar—N=N

D

$-H^+$ ⇅ $+H^+$

$$\left[\begin{array}{c} Cl \\ Cl-Pd \\ Ar-N=N \end{array}\right]^{-}$$

E

$-Cl^-$ ⇅ $+Cl^-$

Cl—Pd
Ar—N=N

F

⇅

DIMER
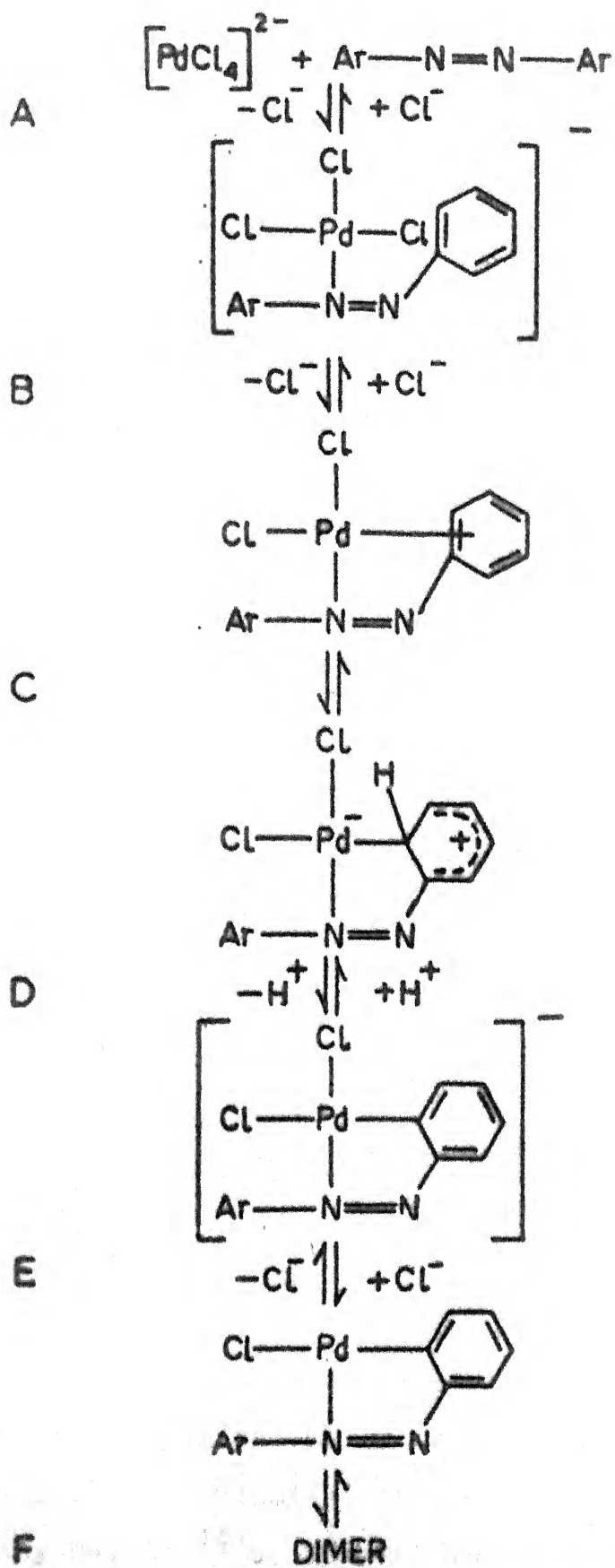
<u>SCHEME 2</u>

solid state[⁽⁾] and this compound is readily converted to the orthobonded complex by heating in solution.

(iv) Olefin, Acetylene and Other Related π-Complexes:

Some of the reactions of the olefin and acetylene complexes of palladium (and also platinum) have been extensively investigated because of their commercial importances. These complexes are involved in many industrial processes viz. Wacker process and hence demand special attention. A few reviews on the olefin and acetylene complexes of palladium and platinum have already been published[141].

Olefins (un) react readily with $Pd(PhCN)_2Cl_2$ in benzene to form complexes of the type $\left[Pd_2Cl_4Un_2\right]$[142] which are less stable than the corresponding platinum complexes. $PdCl_2$ reacts with ethylene in benzene under pressure to give $\left[Pd(C_2H_4)Cl_2\right]_2$[143]. The molecular structure most commonly encountered in these complexes is the halogen bridged dimer XIV[144]. The norbornadiene complex $\left[Pd(Norbornadiene)Cl_2\right]$ has been synthesized by treating Na_2PdCl_4 with norbornadiene in methanol[145]. Treatment of $\left[Pd(PPh_3)_4\right]$ with chloro-olefins yields complexes containing Pd-carbon σ-bonds whereas olefins such as maleic anhydride, ethylfumarate and tetracyanoethylene react to give olefin complexes of zerovalent palladium[146]. The Dewar hexamethylbenzene palladium(II) chloride (structure XV) has been synthesised by Maitlis[147]. Some of the simple alkene-$PdCl_2$ complexes are converted to the π-allyl complexes by treatment
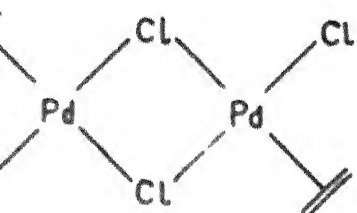
XIV
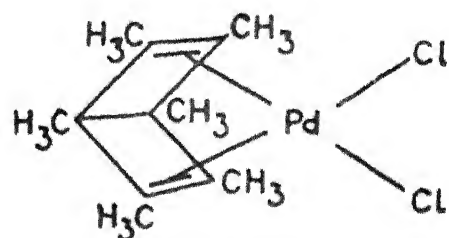
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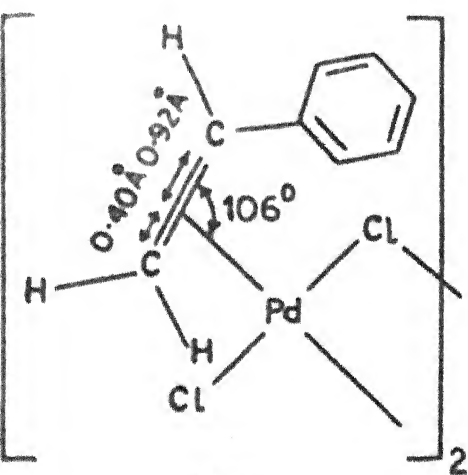
XVI
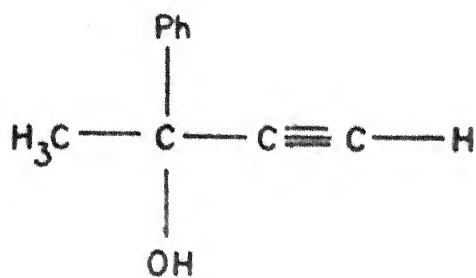
XVII
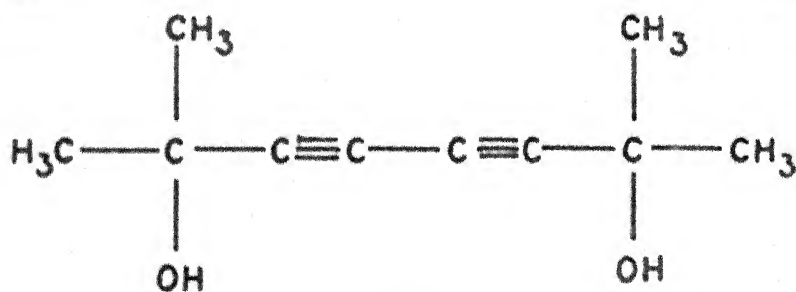
XVIII

at $25^{\circ}C$ with weak bases such as Na_2CO_3, $NaHCO_3$ and Na_2HPO_4[148] or simply by heating above $60^{\circ}C$[149]. Olefins can be recovered from mixtures of gases by forming the Pd(II)-olefin complexes which on heating release the olefins[150]. Pd(II)-complexes have been used in gas chromatography column for separation of olefins.

The structure of $[Pd(PhCH = CH_2)Cl_2]_2$[151], $[Pd(norbornadiene)Cl_2]$[152], $[Pd(1,5-hexadiene)Cl_2]$[153] and $[Pd(cyclooctatetraene)Cl_2]$[154] have been confirmed by x-ray diffraction studies. In the bis-olefin complexes such as dichloro(norbornadiene)palladium(II), dichloro(1,5-hexadiene)-palladium(II) and dichloro(cyclooctatetraene)palladium(II), where the double bonds in the free ligands are parallel, these double bonds lie perpendicular to and symmetrically about the Pd(II)-olefin bond. However, such an arrangement is not essential for the formation of a stable complex as is illustrated by the styrene complex $[Pd(PhCH = CH_2)Cl_2]_2$ (structure XVI) where the double bond is neither symmetrically disposed about the Pd-olefin bond nor perpendicular to the Pd $\underset{Cl}{\overset{Cl}{<}}>$ Pd plane.

The infrared and Raman spectra of Pd(II)-olefin complexes show that the C=C stretching frequency is lowered on coordination to palladium. Since the electron density in the π-bonding orbital of the olefin is substantially reduced on complex formation, olefins coordinated to metal ions are more susceptible to nucleophilic attack (and more resistant to electrophilic attack) than free olefins. Nucleophilic attack on

coordinated mono-olefins is accompanied by the reduction of the divalent metal to the free metal. The fact that metallic palladium can be immediately reoxidised to the divalent state by oxidising agents like benzoquinone or Cu(II) salts had made the catalytic use of palladium salts possible in many organic transformations.

The Pd(II) complexes of acetylene are more complicated and less understood compared to Pt(II) complexes because of the fact that acetylenes are very rapidly polymerised by Pd(II) compounds[155]. The reactions with diphenylacetylene have already been mentioned. Hydroxyacetylenes like XVII and XVIII form stable complexes of the type $\left[PdX(ac)_4\right]$[156] and $\left[Pd(OH)X(acb)\right]$[157] respectively where ac is XVII, acb is XVIII and X = Cl, Br, I and SCN. A brief discussion on acetylene complexes of palladium can be found in the review by Hartley[141].

The carbon disulphide complexes of palladium and platinum $\left[M(PPh_3)_2(CS_2)\right]$ (M = Pd, Pt) can be mentioned in this context since they are the first example of transition metal complexes to exhibit the so-called 'π-CS_2 coordination' i.e. bonding involving a π-bond between the metal and one C=S double bond. These complexes are synthesised by treating $\left[M(PPh_3)_4\right]$ (M = Pd, Pt) with CS_2[158]. X-ray diffraction studies[158,159] have revealed distorted square planar arrangement of donor centers about the metal in each case (structure XIX). The observed bond angle S-C-S (136°) is very close to that found

from spectroscopic methods for the first excited state $(^3A_2)$ of CS_2. The bonding of CS_2 to the metal can therefore be thought of as involving a metal-mediated one electron transfer from the highest π-MO of the ligand to the lowest antibonding MO.

(v) Di-carbollide and Related Sandwich Complexes:

Palladium complexes of 1,2-dicarbollide ions $B_9C_2H_9R_2{}^{2-}$ where R = H or CH_3 have interesting structures. These complexes are formally analogous to the bis(π-cyclopentadienyl) metallocenes. Both the bis(1,2-dicarbollyl) palladium complexes[160,161] and $\left[(\pi-Ph_4C_4)Pd(\pi-B_9C_2H_9Me_2)\right]$[162] have sandwich structures (structure XX). These 1,2-dicarbollyl complexes, which may be written as $\left[Pd^{n+}(1,2-B_9C_2H_{11})_2\right]^{(n-4)}$ are remarkable for their ability of undergoing one-electron transfer reactions to form complexes in which the Pd atom is formally in the +2 (d^8, diamagnetic), +3(d^7, one unpaired electron, 1.68 BM) or +4(d^6, diamagnetic) oxidation state[160]. Two reversible redox couples at $-0.14V$ and $-0.56V$ vs SCE (in acetonitrile with TEAP as supporting electrolyte) were found by controlled potential electrolysis to be each one-electron process. The structures of these complexes, shown schematically in Fig.I have been characterised by careful x-ray diffraction as well as by ^{1}H and ^{11}B nmr studies[160]. The Pd^{IV} (and Ni^{IV}) species are strong Lewis acids, forming crystalline adducts

XIX

Pd
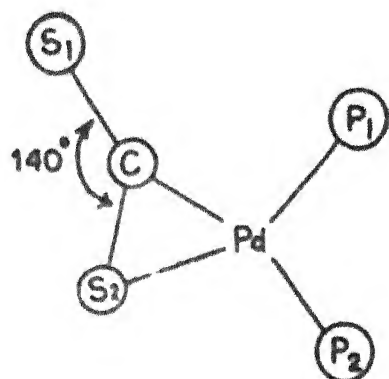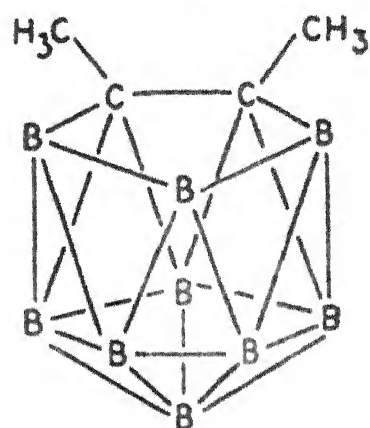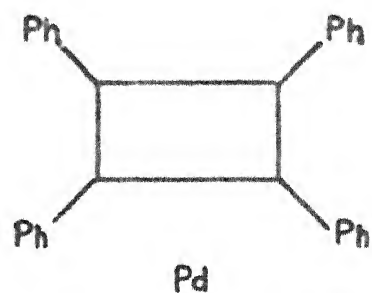
XX
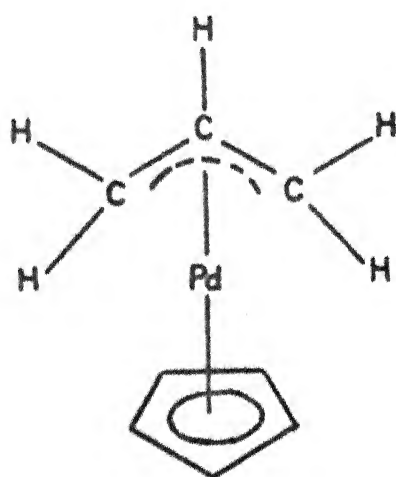
XXI
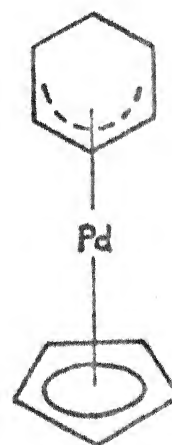
XXII

with certain π and Lewis bases (Cl^-, Br^-, SCN^-, pyrene etc.). The binding in these adducts appears to be primarily a dipole-induced-dipole interaction arising from the high dipole moments of the M^{IV} species.

(vi) π-Allyl Complexes:

Palladium forms a wide range of π-allyl complexes where a three-carbon-atom system donates three electrons to the metal. The π-allyl complexes prepared so far, all involve the metal in +2 oxidation state. These complexes are quite interesting because of their unusual type of bonding and because of their importance as intermediates in the reactions of olefins catalysed by Pd(II) salts. In reactions with olefins, while platinum may form the usual olefin complexes, palladium may form π-allyl complexes as well. The reaction of allyl alcohol with the two metals is one good example:

$$H_2C = CH-CH_2OH + Na_2PtCl_4 \longrightarrow$$

$$Na^+\left[Pt(H_2C=CH-CH_2OH)Cl_3\right]^- + NaCl \qquad \ldots\ldots (7)$$

$$2H_2C=CH-CH_2OH + 2Na_2PdCl_4 \longrightarrow$$

$$\left[(\pi-C_3H_5)PdCl\right]_2 + 4NaCl \qquad \ldots\ldots (8)$$
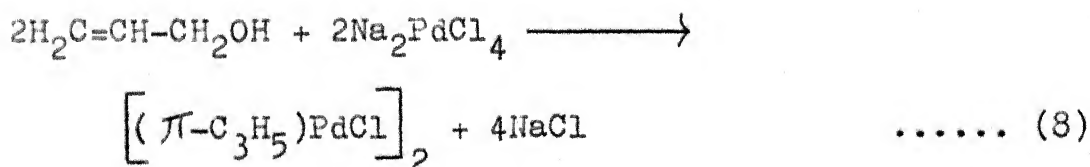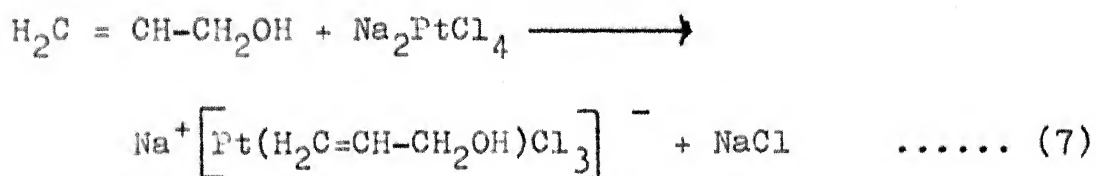
Allyl halides and allyl alcohol are frequently used to synthesise the π-allyl complexes. The parent π-allyl palladium complex $\left[(\pi-C_3H_5)PdCl\right]_2$ can be conveniently prepared

Pd^{II}-'SLIPPED SYMMETRICAL SANDWICH' STRUCTURE (C_{2h} SYMMETRY)
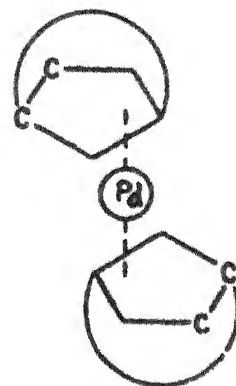
Pd^{III}-'NONSLIPPED SYMMETRICAL SANDWICH' STRUCTURE
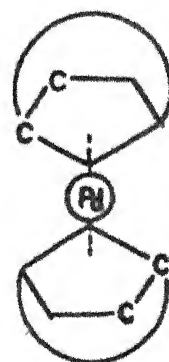
Pd^{IV} -'CISOID SANDWICH' STRUCTURE (C_2 SYMMETRY)
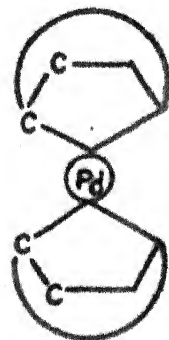
FIG.I. SCHEMATIC STRUCTURES OF $\left[Pd^{n+}(1,2-B_9C_2H_{11})_2\right]^{(n-4)}$

by the reaction between allyl chloride[163] or allyl alcohol[164] and PdCl$_2$ in 50% aqueous acetic acid. Treatment of solution of Na$_2$PdCl$_4$ and one equivalent SnCl$_2$ in methanol with allyl (or substituted allyl) halides give almost quantitative yield of $\left[(\pi\text{-}C_3H_5)PdCl\right]_2$[165]. Olefin complexes of low stability on heating around 100°C, give rise to the more stable π-allyl complexes[163]. Larger alkyl groups on the olefins, presence of a base like sodium acetate and high degree of branching favor the formation of π-allyl complexes in such reactions. With conjugated dienes, π-allyl complexes are also formed with the addition of an extra group to the diene. This new incoming group depends on the solvent used[166]. Tertiary allylamines however, react with Li$_2$PdCl$_4$ in methanol at room-temperature to yield complexes containing Pd(II)-carbon σ-bond[167].

Sandwich π-allyl complexes have also been reported. Treatment of $\left[(\pi\text{-}C_3H_5)PdCl\right]_2$ with cyclopentadienyl sodium gives dark red volatile crystals of $\left[(\pi\text{-}C_3H_5)Pd(\pi\text{-}C_5H_5)\right]$ (structure XXI)[124] whose nmr spectrum confirms the sandwich structure[168]. Similarly cyclopentadienyl sodium reacts with the π-cyclohexenyl Pd complex $\left[(\pi\text{-}C_6H_9)PdCl\right]_2$ to yield $\left[(\pi\text{-}C_6H_9)Pd(\pi\text{-}C_5H_5)\right]$ (structure XXII). The sandwich structure of this complex has also been supported by nmr data[168,169].

π-Allyl palladium complexes have been widely investigated by x-ray diffraction technique[170]. Detailed three dimensional analysis of $\left[(\pi\text{-}C_3H_5)PdCl\right]_2$ at – 140°C[171] indicates

a planar $(PdCl)_2$ bridge and planar C_3H_5 groups with the C_3H_5 and $(PdCl)_2$ planes intersecting at $111.5° \pm 0.9°$ (structure XXIII). At $-140°C$, all the palladium-carbon distances are equal (mean $2.12°A$) and the two π-allyl groups are in an 'anti' configuration. Two other interesting palladium-π-allyl structures that have been determined are the dimeric $\left[(\pi-C_3H_5)Pd(CH_3COO) \right]_2$ (structure XXIV) in which the two π-allyl groups are relatively close together[172] and acetylacetonato(2,4-cyclooctadienyl)-palladium(II) (structure XXV) which is of interest because only three out of five adjacent essentially sp^2 hybridised carbon atoms take part in metal-ligand bonding and the remaining two form a localised double bond[173].

The nmr spectra of π-allyl complexes and their temperature dependence have been extensively studied since they yield a great deal of information on the nature of bonding of the π-allyl group.

The π-allyl complexes like $\left[PdCl(DMSO)_2(CH_2CCl=CH_2) \right]$[174] and $\left[PdCl(PPh_3)_2(CH_2-C(CH_3)=CH_2) \right]$[175] give rise to only one signal for the terminal protons due to a rapid equilibrium

$$CH_2=CH-\overset{*}{C}H_2-Pd \quad \rightleftharpoons \quad \overset{*}{C}H_2=CH-CH_2-Pd$$
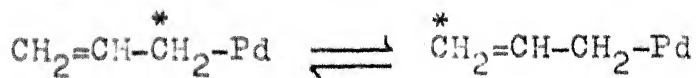
The nmr spectrum of the symmetrical π-allyl complex $\left[(\pi-C_3H_5)PdCl \right]_2$ at low temperature in a noncoordinating solvent like $CDCl_3$ consists of three sets of peaks (AA'BB'X spectrum) with τ values H_+ 4.55, H_β 5.98 and H_α 7.05[168]. At high temperatures (which vary from system to system) and in the presence of a coordinating solvent or added ligand
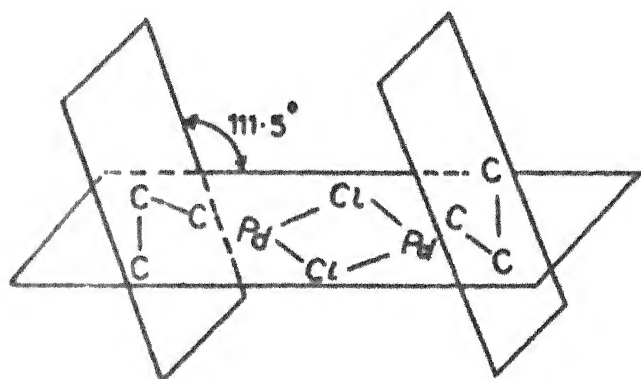
XXIII
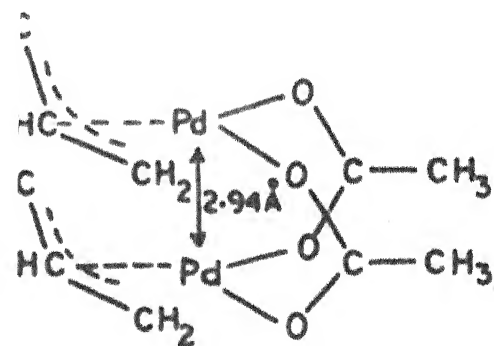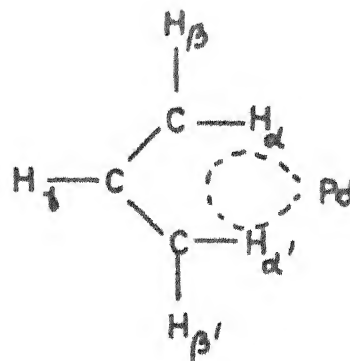
XXIV
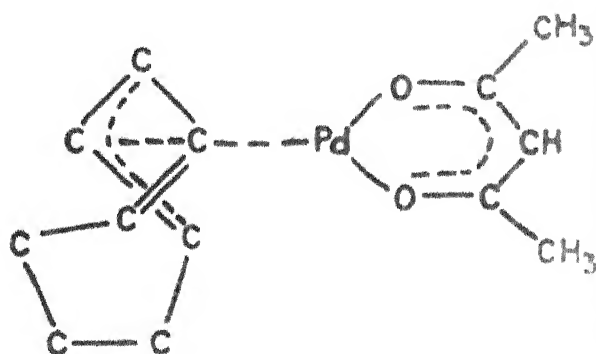
XXV
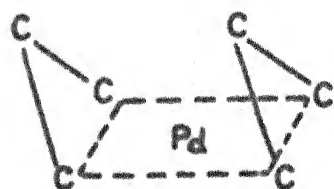
XXVI
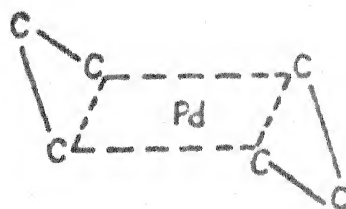
XXVII

like PPh_3, the AA'BB'X spectrum collapses to an A_4 X spectrum by coalescence of the H_α and H_β peaks in a single peak indicating the equivalence of the four terminal protons. At a very low temperature, asymmetric π-allyl complexes such as $\left[(\pi-C_3H_5)PdCl(PPh_3)\right]$[175] exhibit ABCDX spectra due to the non-equivalence of H_α and H_α' as well as H_β and H_β' protons which results from their being _trans_- to two different ligands. The pmr spectrum of $\left[Pd(\pi-C_3H_5)_2\right]$ at low temperature consists of two AB_2C_2 spectra present in unequal amount which has been interpreted in terms of an equilibrium mixture of _syn_- and _anti_-isomers (structure XXVI and XXVII)[176].

The π-allyl complexes may be described as "stereochemically non-rigid" systems. From the temperature dependence of their nmr spectra, different kinds of motions of the coordinated π-allyl groups in palladium complexes have been suggested[177].

Infrared and Raman spectra of π-allyl complexes have been used chiefly to demonstrate the absence of C=C vibration present in the free allyl ligand[178]. A detailed investigation of the electronic spectra of $\left[(\pi-C_3H_5)PdCl\right]_2$ in different solvents has been done by Hartley[179].

I.2.D +4 Oxidation State

The number of palladium(IV) compounds and complexes is quite less as compared to those of tetravalent platinum;

this is largely due to the much higher ionisation energy needed to produce Pd^{+4} than Pt^{+4} ions. The observed configuration is octahedral (or nearly octahedral) and all the compounds and complexes of tetravalent palladium are diamagnetic.

The oldest compound reported to contain tetravalent palladium is $\left[Pd_2(NH)_3)_4Cl_6\right]$[180] which consists of vertical stacks of alternate Pd(II) and Pd(IV) ions separated by halide bridging ligands. The highest filled d-orbital of a Pd(II) ion (probably d_z2 since in such complexes the ligands are purely σ-bonding) and the empty d_z2 orbital of the adjacent Pd(IV) ion overlap via the 3p orbital of the intervening chloride ion and this results a strong polarisation along the metal atom chain. That the electrical conductivity of $\left[Pd^{II}(NH_3)_2Cl_2\right]\left[Pd^{IV}(NH_3)_2Cl_4\right]$ is 500 times greater in the direction of $-Cl-Pd^{II}-Cl-Pd^{IV}-Cl-$ chains than perpendicular to them[181] is consistent with this overlap scheme. Another similar compound $\left[PdPt(NH_3)_4Cl_6\right]$ containing alternate bivalent palladium and tetravalent platinum has been well-characterised by x-ray diffraction study[182]. The resonance Raman spectra and far-infrared spectra of $\left[Pd_2(NH_3)_4Cl_6\right]$ and $\left[PdPt(NH_3)_4Cl_6\right]$ have been studied by Clark[183].

The only stable complex of tetravalent palladium with ligands containing group IVB elements as donors is $K_2Pd(CN)_6$. This complex is obtained by treating K_2PdCl_6 with KCN in presence of a strong oxidising agent like potassium peroxydisulphate[184]. The few amino-Pd(IV) complexes known so far

include $\left[Pd(NH_3)_2Cl_4\right]$, $\left[Pd(en)Cl_4\right]$ and $\left[Pd(py)_2X_2Cl_2\right]$ where

X = Cl, Br or I. All the complexes have been synthesised by

oxidising the corresponding dichloropalladium(II) complexes

with halogens in chloroform solution. The tertiary phosphine

and tertiary arsine complexes of tetravalent palladium and

platinum have also been prepared by the oxidation of the

corresponding divalent metal complexes by halogens.

$\left[Pd(diars)_2X_2\right]$ where X = Cl or Br and diars = O-phenylenebis

(dimethylarsine), on oxidation with nitric acid yield the

stable complex ion $\left[Pd(diars)_2X_2\right]^{2+}$ whose perchlorate salt can

be readily isolated on addition of perchloric acid[185].

Tetravalent palladium form binary oxide, sulphide,

selenide and telluride. Palladium disulphide and diselenide

have elongated pyrites structure in which the palladium atom

is surrounded by four chalcogen atoms in a square plane

($Pd-S = 2.30°A$ in PdS_2) with two more chalcogen atoms at a

slightly greater distance[186]. This distortion splits the

degeneracy of the e_g level and the compounds are diamagnetic

semiconductors[187]. On increasing pressure, the axial sulphur

atoms in PdS_2 come closer to the metal leading to a semicondu-

ctor to metallic conductor transition[188]. $PdTe_2$ is a super-

conductor below 1.69K[189] and has cadmium iodide structure.

All the binary chalcogenides except the oxide, are prepared

by heating $PdCl_2$ with excess chalcogens at elevated temperatures

(400-750°C)[190]. The hydrated oxide PdO_2, nH_2O is formed as a

dark red precipitate by treating M_2PdCl_6 (M = K, Na) with alkali[191]. When heated around 200°C, the compound loses oxygen to yield PdO.

The only known simple halide of tetravalent palladium is PdF_4. This brick red crystalline compound is synthesised by heating $Pd^{II}\left[Pd^{IV}F_6\right]$ with fluorine at 150-300°C[192]. X-ray diffraction data of the powder shows a tetragonal unit cell (a = 6.585°A, c = 5.835°A) with four formula units in the cell[192]. The complex halides of tetravalent palladium are all well-characterised. The compound, originally thought to be PdF_3 is actually $Pd^{II}\left[Pd^{IV}F_6\right]$. This black crystalline solid which can be obtained by fluorinating PdX_2 (X = halogen) at 200-250°C in a flow-system[193] has magnetic moment (at room temperature) corresponding to two unpaired electrons associated with Pd^{+2} in an octahedral environment[192]. X-ray diffraction study of the powdered sample shows Pd-F=2.04°A in $\left[PdF_6\right]^{2-}$ [194]. Apart from $\left[PdF_6\right]^{2-}$, two other complex halides namely $\left[PdCl_6\right]^{2-}$ and $\left[PdBr_6\right]^{2-}$ are known and the increasing stability order is $PdF_6^{2-} < PdCl_6^{2-} < PdBr_6^{2-}$. These complex halides are generally prepared by the action of halogens on the divalent metal halide complexes dissolved in the corresponding hydraacids. The electronic spectra of the complex halides of palladium and platinum) have been analysed and assigned by Henning et al.[195] X-ray diffraction studies have shown that all these complex halides of tetravalent palladium are isostructural

with $(NH_4)_2PtCl_6$ with the metal atom octahedrally surrounded
by the halogen atoms[194,196].

I.3 OBJECTIVE OF THE PRESENT INVESTIGATION

Arylazooximes XXVIII have an interesting coordination
chemistry. Many years ago, Feigl[197] studied the "Salt-forming"
ability of phenylazoacetaldoxime with copper(II). He succeeded
in isolating some green copper complexes that were insoluble in
ammonia but soluble in organic solvents. Hunter and Roberts[198]
first observed that arylazooximes undergo fast reactions with
cobalt(II) acetate in alcohol producing purple tris-complexes
of trivalent cobalt. They suggested without any substantial
evidence a six-membered chelate ring XXVIII. Malatesta and
Pizzoti[199] described the diamagnetic bis-complexes of nickel(II)
which they formulated as XXIX with five-membered chelate rings,
apparently on the basis of analogy with the structure of bis-
(dimethylglyoximato)nickel(II). Work from this laboratory
during past years has systematised the coordination chemistry
of arylazooximes to a considerable extent. The present work
deals with the arylazooximates of palladium and to a limited
extent with those of platinum.

The arylazooximes are obtained[200,201] by nitrosation of

arylhydrazones of aldehydes with n-butylnitrite:

$$\text{R-C=N-NHAr} \quad \xrightarrow{\underline{n}\text{-}C_4H_9ONO} \quad \text{R-C-N=N-Ar}$$

with H below the first structure and NOH below the second.
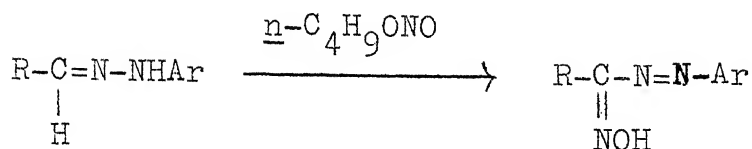
(R = alkyl or aryl, Ar = aryl)   XXVIII

Previous work from this laboratory[201,202] has shown that arylazooximes are extensively bydrogen-bonded and exhibit cis-trans isomerism around C=N in solution. In what follows the ligand with Ar=C_6H_5 will be abbreviated as HRaao and its conjugate base $\left[\text{R-C(=NO)-N=N-Ar} \right]^-$ as Raao$^-$. Arylazooximes in which Ar group is different from C_6H_5 are not considered here for the sake of brevity.

The report of Hunter and Roberts initiated detailed studies on the nature of coordination, size of the chelate rings and the possibility of cis-trans isomerism in the tris complexes. The infrared, electronic and pmr spectra of Co(Raao)$_3$[203] and Rh(Raao)$_3$[204] were studied very carefully. The chelate rings were concluded to be five-membered XXX. The stereochemistry in the cobalt(III) complexes are exclusively trans XXXI while the rhodium(III) complexes exist in both cis XXXII and trans form. The observed stereochemistries are rationalised on the basis of ligand steric hindrance and size of the metal ion[203,204]. The dinuclear copper(II) species of the type Cu$_2$(Raao)$_4$ are strongly exchange-coupled and are
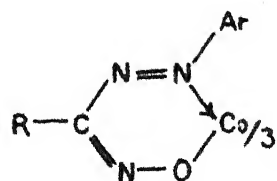
XXVIII
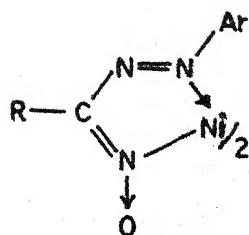
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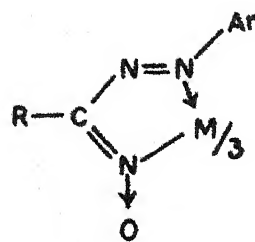
XXX
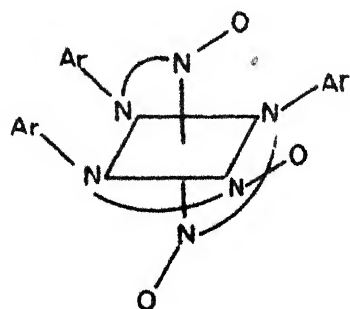
XXXI
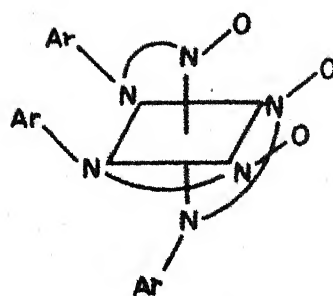
XXXII

XXXIII
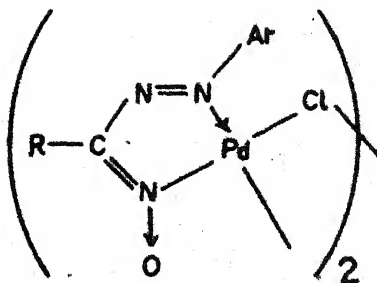
XXXV

XXXIV

diamagnetic both in solid state and in solution[205]. In course
of the work with arylazooximes the reaction of cobalt salts
with the phenylhydrazone of ω-nitroacetaldehyde[203] and the
instantaneous oxidation of β-(α-oximinoethyl)phenylhydrazine
by oxygen in the presence of Cu^{2+}, Co^{2+} and Pd^{+2} to arylazo-
oximes[205] have also been studied. Arylazooximes have strong
affinity for iron(II). The α-azoimine group XXXIII present
in arylazooximes is isoelectronic with the α-diimine
function XXXIV which strongly binds iron(II). The tris-**complex**
$Fe(Raao)_3^-$ can be readily obtained in the form of the sodium
salt[206] $NaFe(Raao)_3 \cdot H_2O$ in which the $Fe(Raao)_3^-$ moiety has
cis-geometry (pmr data). The sodium ion is believed to be
bound to the water molecule and to oxime oxygen atoms.
$NaFe(Raao)_3 \cdot H_2O$ is poorly conducting in nitromethane solution
and soluble in organic solvents. On reacting with acids, it
produces $HFe(Raao)_3$ in which the proton is believed to be
chelated to $Fe(Raao)_3^-$ via the oxime oxygen atoms. Reaction
of HRaao with $FeCl_3$ produces a crystalline solid which has
been shown[207] to be an intervalence species of the type
$\left[Fe^{III}(Fe^{II}(Raao)_3)_2\right]Fe^{III}Cl_4$. In this compound both iron(III)
atoms are high-spin. The iron(III) atom in the cation is most
probably bound in an octahedral fashion to the six oximato
oxygen atoms of the two cis- $Fe(Raao)_3^-$ moieties. The
corresponding perchlorate $\left[Fe^{III}(Fe^{II}(Raao)_3)_2\right]ClO_4$ is obtained
by a direct reaction between iron(II) perchlorate and Haao.

The chemical conversion of the various species are also well-studied[207]. The $\left[Fe(Fe(Raao)_3)_2 \right] X$ ($X = ClO_4$, Br) shows a $g \sim 4.3$ epr line characteristic of rhombic FeO_6 sphere. When $X = FeCl_4^-$, and intense additional band at $g \sim 2.0$ (due to $FeCl_4^-$) is also observed[207].

In view of the interesting results obtained with several metal ion, we felt it worthwhile to investigate the interaction of HRaao with palladium and platinum. A beginning in this direction was made sometime ago when the bridged system XXXV was discovered[204]. The bridge-splitting and ring-opening reactions of the halogen-bridged palladium(II) aryl-azooximates, the nature of the bis-complexes, the interconver-tions of the different types of species, the redox reactions with halogens are a few of the topics that are investigated. The results of these and related investigations constitute the bulk of the present thesis. At present, the platinum-Raao chemistry is less well-developed than the corresponding palladium-Raao chemistry.

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CHAPTER II

DI-μ-HALOBIS $\left[\text{ARYLAZOOXIMATOPALLADIUM(II)}\right]$,

BIS(ARYLAZOOXIMATO)PALLADIUM(II) AND RELATED SPECIES:

SYNTHESIS,STRUCTURE AND INTERCONVERSION.

CHAPTER II

DI-μ-HALOBIS [ARYLAZOOXIMATOPALLADIUM(II)], BIS(ARYLAZOOXIMATO)PALLADIUM(II) AND RELATED SPECIES: SYNTHESIS, STRUCTURE AND INTERCONVERSION.

Abstract: Arylazooximes R-C(=NOH)-N=N-Ar (HRaao), form two types of complexes with palladium namely the halo-bridged arylazooximates $Pd_2(Raao)_2X_2$ and the bis-arylazooximates $Pd(Raao)_2$.   Various synthetic methods have been reported for the two types of complexes. Probable pathways of the synthetic reactions are discussed. The interconversion routes between the two types of complexes are also described. Novel mixed species viz Pd(Raao)(R'aao) and Pd(Raao)(azbz) have been synthesised. The N-O stretching frequency in the infrared spectra of palladium(II) arylazooximates appears in the region 1220-1280 cm^{-1} The high energy shift indicates a five-membered chelate ring with nitrone structure. A trans-formulation has been proposed for the bis-complexes. The moiety (Raao)Pd invariably exhibits an intense band at ∿ 500 nm with an extinction coefficient of ∿ 5000 per Pd atom. This band probably arises from a metal ⟶ ligand charge transfer. In the case of bis-complex,

an intense band with a double-humped structure appears at a relatively lower energy region ($\sim$ 600 nm). The methyl signal of the chelated arylazooximato fragment in Pd(Meaao)$_2$ and Pd(Meaao)(azbz) appears at δ = 2.31 and 2.4 ppm respectively.

II.1 INTRODUCTION

The major part of the investigation described in this thesis concerns the various facets of the chemistry of two types of palladium compounds namely the halo-bridged arylazo-oxime complexes and the halogen-free bis-arylazooximates. In this chapter, some synthetic and structural aspects of these two types of complexes are presented.

Preliminary work on arylazooximates of palladium was initiated in this laboratory some time ago[1]. The initial stimulus was provided by the work of Cope and Siekman[2] who reported that prolonged reaction of azobenzene with K_2MCl_4 (M = Pd, Pt) in dioxane-water mixture gives rise to halobridged orthometallated products. Arylazooximes have, apart from the oxime function, an arylazo group. Therefore, the initial interest was to find whether a similar metallation of the phenyl ring can occur in the reactions of arylazooximes with K_2PdCl_4. It was found that arylazooximes undergo fast reactions with K_2PdCl_4 in aqueous alcohol medium to form a class of chloro-bridged dinuclear complexes which on the basis of infrared and other data were given the structure I[1]. In no case metallation of the phenyl

I
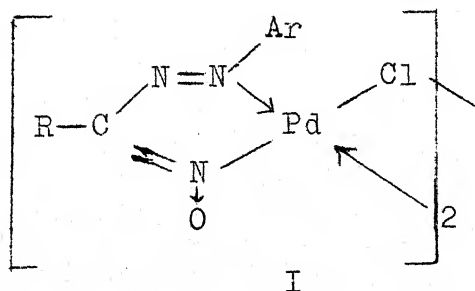
R = alkyl or aryl, Ar = aryl.

ring occurs. Evidently the deprotonation and binding by oximato nitrogen to palladium is a much more facile process than the deprotonation and binding by an aromatic CH fragment.

For the sake of completeness the abbreviations used (already described in Chapter I) are restated here before we pass on to results and discussions. R-C(=NOH)-N=N-Ar is abbreviated as HRaao where H refers to the dissociable oxime proton.

Other abbreviations used frequently in the following sections and forthcoming chapters are

Me	methyl
Et	ethyl
Ph	phenyl
o-tol	ortho-tolyl
m-tol	meta-tolyl
p-tol	para-tolyl
Bu^t	tert-butyl
Cy	cyclohexyl
bz	benzene
chl	chloroform
aq	aqueous
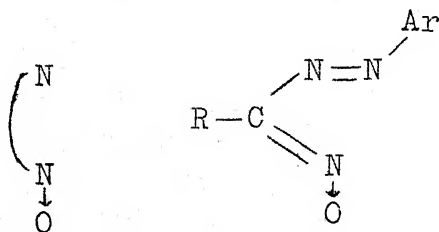
II.2   RESULTS AND DISCUSSION

A.   Synthetic Experiments

a. Chloro-bridged Arylazooximates

It was already noted that K_2PdCl_4 (aqueous solution) undergoes an extremely facile 1:1 reaction with arylazooximes (in ethanol) producing the complexes I[1]. One of the major disadvantages of this method is that, with arylazooximes having R = aryl, the products are always appreciably contaminated with bis-arylazooximates of the type $Pd(Raao)_2$. Tedious and repeated washings with benzene are needed to remove the $Pd(Raao)_2$ impurities. As will be stated later, this contamination arises from the presence of water in the reaction mixture. We now report a few general procedures which always yield pure chloro-bridged complexes. The first procedure involves bis(benzonitrile)-palladium(II) chloride $Pd(PhCN)_2Cl_2$ as the starting palladium compound. $Pd(PhCN)_2Cl_2$ reacts readily with arylazooximes (in the molar ratio 1:1) in ethanol or benzene to produce pure chloro-bridged arylazooxime complexes I irrespective of the nature of the R group:

$$2\ Pd(PhCN)_2Cl_2 + 2\ HRaao \xrightarrow{\text{EtOH or bz}} I + 2\ PhCN + 2HCl \ \ldots (1)$$
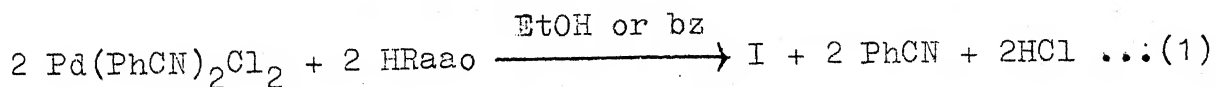
Bis(benzonitrile)palladium(II) chloride $Pd(PhCN)_2Cl_2$, first reported by Kharasch[3] is a loose complex of palladium which is soluble in organic solvents. Quite a few syntheses[3,4] are known where this complex has been used as the starting

palladium compound. In solution Pd(PhCN)$_2$Cl$_2$ slowly looses

benzonitrile and PdCl$_2$ is ultimately deposited[5]. Thus in

effect, Pd(PhCN)$_2$Cl$_2$ is a source of PdCl$_2$ which can be used

in organic solvents. Since this synthesis is devoid of water,

contamination of the product by Pd(Raao)$_2$ does not occur at all.

The success of the above method initiated us to try

PdCl$_2$ as the starting palladium compound. And in fact arylazo-

oximes do react with PdCl$_2$ in boiling ethanol (in molar

ratio 1:1) to yield pure chloro-bridged arylazooximates I even

when R = aryl. An immediate characteristic violet color is

developed when PdCl$_2$ is added to the ethanolic solution of

phenylazoacetaldoxime; the whole amount of PdCl$_2$ dissolves

smoothly in the ethanolic solution at room temperature and

finally di-μ-chlorobis[phenylazoacetaldoximatopalladium(II)]

crystallises out. Arylazooximes with R = aryl, however, react

slowly with PdCl$_2$. The reaction is hastened by boiling the

ethanolic solution of arylazooxime with PdCl$_2$ to reflux for

1-2 hours. In each case the pure chloro-bridged complex is

isolated in $\sim$ 85% yield.

Another general method which yields pure chloro-bridged

arylazooximates involves the reaction between Pd(Raao)$_2$ and

dichlorine. The green solutions of bis-arylazooximates

Pd(Raao)$_2$ in benzene, when exposed to dichlorine for a short

time, turn clear red. The amount of dichlorine should be just

sufficient to bring about the color-change but no precipitation.

Excess dichlorine leads to a complicated reaction resulting in deposition of $PdCl_2$ and unidentified organic products. After the clear red solutions are carefully concentrated, addition of ethanol to them brings about the diposition of the chloro-bridged complexes I:

$$Pd(Raao)_2 \text{ in bz} \xrightarrow{Cl_2} \text{Deep red solution}$$

Pd(Raao)$_2$ in bz
green

concentrated
and
EtOH added

$$Pd_2(Raao)_2Cl_2 + 2HRaao \qquad \dots (3)$$

I
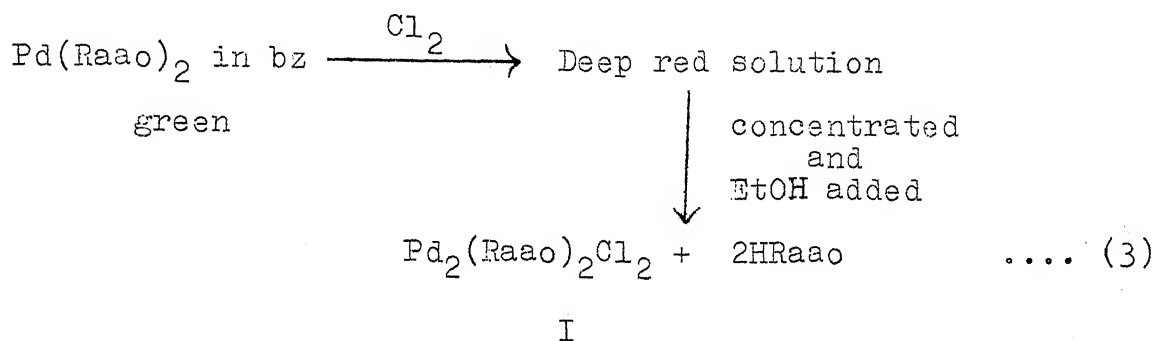
In the above synthesis with R = aryl, the chloro-bridged complexes start separating out even while concentrating the red solutions. The nature of the species formed initially in this reaction will be discussed in detail in Chapter V. Most possibly the initial reaction is an oxidation leading to an unstable Pd(IV) species which subsequently react with ethanol to produce the chloro-bridged complexes. Addition of ethanol to the red solutions serves several purposes. First, the conversion of $Pd(Raao)_2$ to $Pd_2(Raao)_2Cl_2$ is accompanied by rejection of one ligand per Pd atom which remains soluble in the alcoholic medium. Second, since the chloro-bridged complexes are sparingly soluble in alcohol, ethanol acts as a precipitating agent. And third, ethanol which is known to act as a reducing agent, possibly reduces the unstable Pd(IV) species back to bivalent palladium. In the reaction with

R = aryl, the Pd(IV) species in the red solutions are probably thermally unstable and hence the chloro-bridged complexes start separating out even before the addition of ethanol. The addition, however, completes the precipitation.

b. Bromo-bridged Arylazooximates

Conversions of the chloro-bridged complexes to the corresponding bromo-bridged complexes were earlier achieved by reaction with LiBr in acetone[1,6] (vide experimental section):

$$I \xrightarrow{\text{LiBr in} \atop \text{acetone}} \left[\begin{array}{c} R-C \underset{\underset{O}{\overset{\displaystyle N}{\downarrow}}}{\overset{\displaystyle N=N}{}} \underset{\text{Ar}}{\overset{}{}} Pd \underset{}{\overset{\text{Br}}{}} \end{array} \right]_2 + \text{LiCl} \qquad \dots (4)$$

II
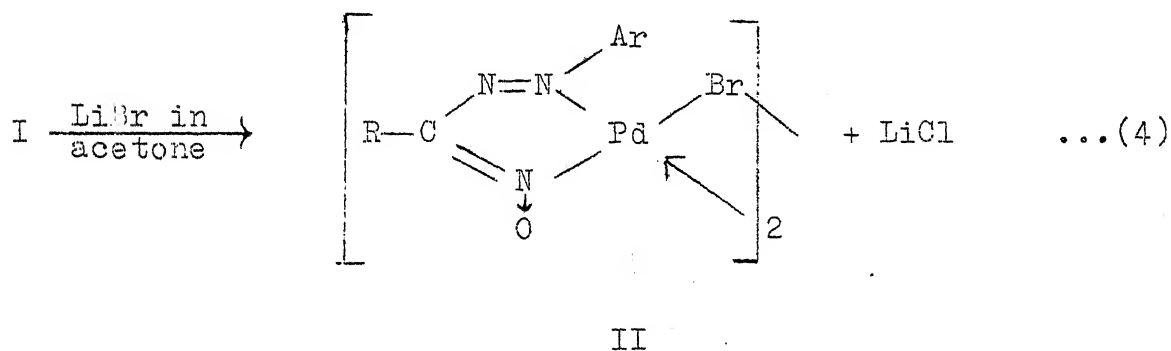
New general methods developed in course of the present study parallel to those used for chloro-species and include

(i) Reaction between aqueous K_2PdBr_4 and HMeaao in ethanol.

(ii) Reaction between $Pd(Raao)_2$ and dibromine (molar ratio 1:1) in benzene.

(iii) Reaction of $Pd(PhCN)_2Br_2$ with HRaao in ethanol (molar ratio 1:1).

and (iv) 1:1 reaction between $PdBr_2$ and HRaao in boiling ethanol.

The observations and results obtained in these methods are closely analogous to those found in the corresponding syntheses of the chloro-species. Reaction (i) is quite facile whereas reaction (iii) is not so and needs heating to $60^{\circ}C$ for a quick completion (within 10 minutes). Excess dibromine in reaction (ii) leads to deposition of $PdBr_2$ and unidentified organic products. In the 1:1 reaction between $Pd(PhCN)_2Br_2$ and HRaao (R = aryl) in benzene at room temperature, bright red crystals of III separate out which in contact with moisture or alcohol are readily converted to II:

$$Pd(PhCN)_2Br_2 + HRaao \xrightarrow{\ bz\ }$$

R = aryl

III

moisture
or
EtOH

$$Pd_2(Raao)_2Br_2 \qquad ...(5)$$

II
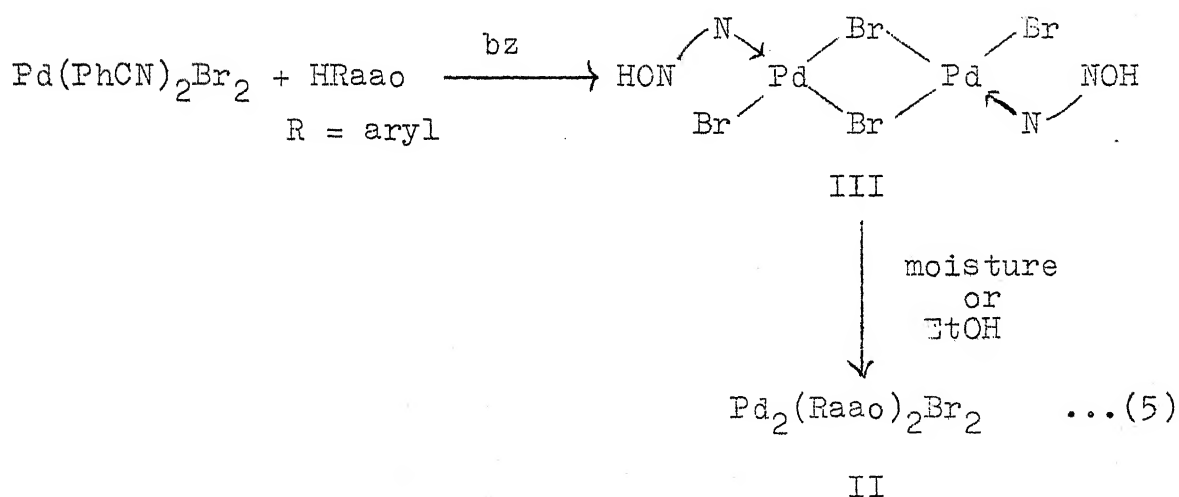
Thus $Pd(PhCN)_2Br_2$ reacts with HRaao (R = aryl, molar ratio 1:1) in benzene containing a little ethanol or in pure ethanol to produce II. In III arylazooximes most possibly act as monodentate ligands bound to palladium through the azo-ends only (vide infra).

The halo-bridged complexes are all violet to purple crystalline solids which are soluble in benzene, chloroform and dichloromethane. Complexes with R = aryl are sparingly soluble. For Ar = C_6H_5, the following order of increasing solubility is observed: p-tol $<$ Ph $<$ Me (these groups refer to R).

c. Bis-arylazooximates

K_2PdX_4 reacts with arylazooximes (having R = aryl) in the molar ratio 1:2 in AQUEOUS ethanol to produce the bis-arylazooximates $Pd(Raao)_2$:

$$K_2PdX_4 + 2 \text{ HRaao} \xrightarrow{\text{aq EtOH}}$$

$$+2HX+2KX$$

$$(X = Cl, Br)(R = aryl) \qquad\qquad\qquad ....(6)$$
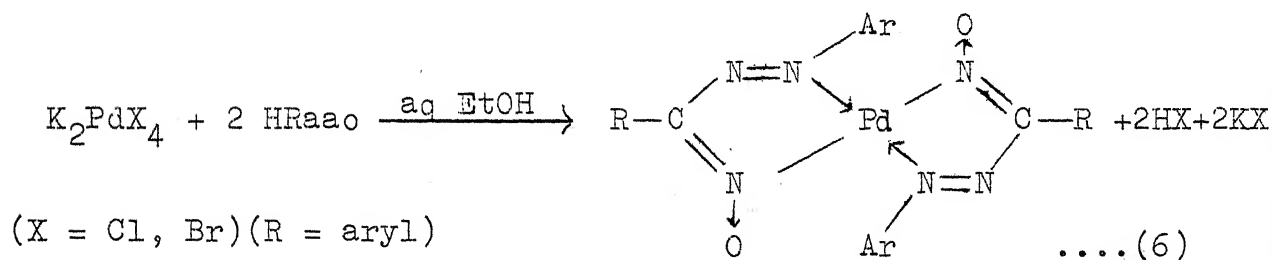
IV

In the usual syntheses of halo-bridged arylazooximes I and II starting from K_2PdX_4 and arylazooximes with R = aryl, these bis-arylazooximates are also formed along with the desired complexes I and II. The products are then washed throughly with benzene when the bis-complexes are collected in the washings and they can be crystallised out by adding hexane to the concentrated washings. When R = CH_3 i.e. with phenyl-azoacetaldoxime, the ratio of metal to ligand needed for the formation of bis-complex is about 1:4. In this method, the

halo-bridged complexes are formed initially which further react with one mole of respective arylazooxime in presence of water to yield the bis-complexes IV:

$$K_2PdX_4 \xrightarrow[\text{aq EtOH}]{\text{HRaao}} Pd_2(Raao)_2X_2 \xrightarrow[\text{aq EtOH}]{\text{HRaao}} Pd(Raao)_2 \qquad ...(7)$$

$$\text{I, II} \qquad\qquad\qquad \text{IV}$$
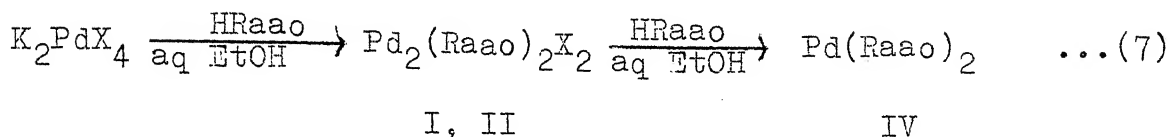
This observation suggests a very simple method of obtaining bis-complexes from the halo-bridged ones (vide section II.2.A.d). $Pd(PhCN)_2Cl_2$ also reacts with two moles of arylazooximes in AQUEOUS ethanol to produce IV.

The presence of water is a necessary condition for the formation of the bis-complexes. This fact was established by the following observations:

(i) $K_2PdCl_4 + 2HPhaao \xrightarrow{\text{aq EtOH}} Pd(Phaao)_2 + 2HCl + 2KCl$

(ii) $Pd(PhCN)_2Cl_2 + 2HPhaao \xrightarrow{\text{aq EtOH}} Pd(Phaao)_2 + 2PhCN + 2HCl$

$\qquad Pd(PhCN)_2Cl_2 + 2HPhaao \xrightarrow{\text{bz or chl}}$ Red solution

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ ↓ poured into
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ water; stir

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $Pd(Phaao)_2$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (green organic layer)

(iii) $Pd_2(Phaao)_2Cl_2 \xrightarrow[\text{2. heat}]{\text{1. poured into water, stir}}$ No change

(iv) $Pd_2(Phaao)_2Cl_2 + 2HPhaao \xrightarrow[\text{chl}]{\text{bz or}}$ Red solution

$\downarrow$ poured into
water; stir.

$Pd(Phaao)_2$

(green organic layer)

(v) $Pd(PhCN)_2Cl_2 \xrightarrow[\text{added slowly}]{\text{HPhaao in bz}} Pd_2(Phaao)_2Cl_2$

in bz

(purple ppt)

$\downarrow$ add^n of HPaao
continued till
Pd: HPhaao=1:2

$Pd(Phaao)_2 \xleftarrow[\text{water}]{\text{poured into}}$ Clear red solution

$\downarrow$ kept for $\frac{1}{2}$ hr

Vermillion red ppt

$\downarrow$ moist air

$Pd_2(Phaao)_2Cl_2$

(violet)

The nature of the species in the red solution (reaction ii, iv
and v) and that of the vermillion red precipitate (reaction v)
will be described in detail in Chapter IV and V. Suffice it to
state that the vermillion red compound is most possibly
$Pd_2(HPhaao)_2Cl_4$ with structure V in which HPhaao is bonded to
palladium only through the azo-end. In the presence of

moisture (which acts as a base) the ligands get deprotonated and chelate rings are formed with the elimination of Cl⁻ ion:

$$\text{V} \xrightarrow[\text{$-2H^+$; $-2Cl^-$}]{\text{moisture}} \underset{\substack{\text{I} \\ \text{(R=Ph)}}}{Pd_2(Raao)_2Cl_2} \quad \ldots.(8)$$

The role of water in the reactions leading to the syntheses of bis-complexes is clear from the above observations. The first step in the syntheses of bis-complexes is the formation of halo-bridged arylazooximates. Several Lewis bases split the halogen bridge (Chapter III) and likewise arylazo-oximes are also capable of doing so. We have shown that azobenzene cannot split the bridge in I; azo-nitrogens are not strong enough coordinating centers. The halogen-bridge is most probably split by the oxime-end of the second molecule of arylazooxime. Subsequent elimination of proton and halide ion and chelate formation through the azo-end produce the bis-complex. The presence of a base helps the elimination of protons and thus facilitates the formation of $Pd(Raao)_2$.

Step 1
$$\left. \begin{array}{l} K_2PdX_4 \\ \text{or } Pd(PhCN)_2X_2 \\ \text{or } PdX_2 \end{array} \right] + \text{HRaao} \longrightarrow \underset{\text{I}}{Pd_2(Raao)_2X_2}$$

Step 2   I $\xrightarrow{\text{HRaao}}$

VI

$$\downarrow \quad -H^+; \; -X^-$$

Pd(Raao)$_2$

IV

The formation of bis-complexes in the syntheses of halo-bridged complexes with arylazooximes having R = aryl is also clear. Since these halo-bridged complexes are sparingly soluble in aqueous ethanol, they start separating out with the addition of ligands. And once some halo-bridged product accumulates, a side reaction starts between the halo-bridged complex and arylazooxime in aqueous ethanol leading to the formation of the bis-complex. Thus while K$_2$PdX$_4$ reacts with arylazooxime to produce the desired halo-bridged complex, part of the product reacts further with arylazooxime to produce the bis-complex also. In effect, in these reactions, some palladium is left in the solution phase since Pd:HRaao ratio used is 1:1. In the case of HMeaao the halo-bridged complex is quite soluble in alcohol and moreover it reacts only with excess arylazooxime (Pd: HMeaao ratio ∼ 1:4) to produce the bis-complex. Hence the synthesis of halo-bridged complex of

phenylazoacetaldoxime gives neat product. The reason behind the difference in the reactivity of arylazooximes with R = aryl and R = alkyl might be related to the acidity of the = NOH group.

Water is not the only base which brings about the reaction between $Pd_2(Raao)_2X_2$ and arylazooximes leading to the formation of the bis-arylazooximates. It has been shown[1] that the halo-bridged arylazooximates I and II react with corresponding arylazooximes (in the molar ratio 1:2) in presence of suspended sodium carbonate in benzene to produce the bis-arylazooximates $Pd(Raao)_2$.

Another starting palladium compound which can be used in the synthesis of the bis-arylazooximates is bis(salicyl-aldehydo)palladium(II), $Pd(Sal)_2$. $Pd(Sal)_2$ reacts readily with two equivalents of arylazooximes in benzene at room temperature to produce the bis-complexes $Pd(Raao)_2$:

$$Pd(sal)_2 + 2HRaao \xrightarrow{bz} Pd(Raao)_2 + 2HSal \qquad \dots \ (9)$$
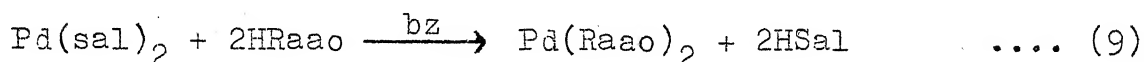
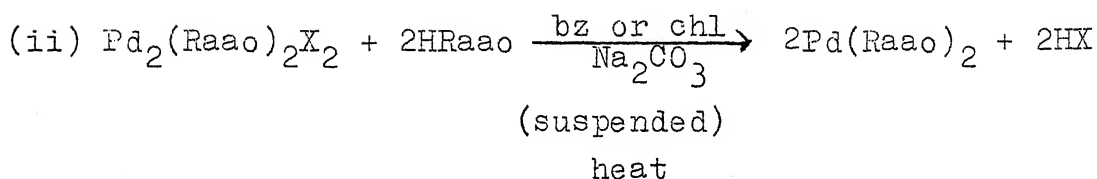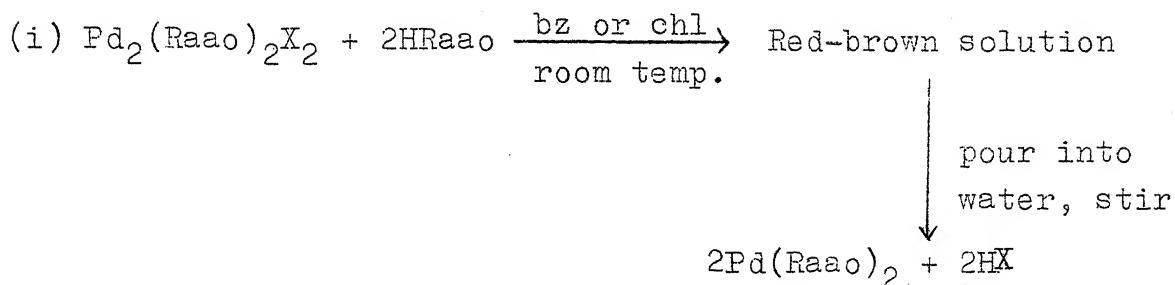The bis-complexes are all dark crystalline solids soluble in benzene and chloroform to give **green** solutions. Here also for Ar = C_6H_5, the order of increasing solubility is p-tol$<$Ph$<$Me (these groups refer to R).

d. Interconversions

The interconversions of the two types of complexes namely $Pd(Raao)_2X_2$ and $Pd(Raao)_2$ are apparent from their modes of

synthesis. Conversions of $Pd_2(Raao)_2X_2$ to $Pd(Raao)_2$ have been achieved in the following two ways:

(i) $Pd_2(Raao)_2X_2$ + 2HRaao $\xrightarrow[\text{room temp.}]{\text{bz or chl}}$ Red-brown solution

$\downarrow$ pour into water, stir

$2Pd(Raao)_2$ + 2HX

(ii) $Pd_2(Raao)_2X_2$ + 2HRaao $\xrightarrow[Na_2CO_3]{\text{bz or chl}}$ $2Pd(Raao)_2$ + 2HX

(suspended)

heat

The probable mechanisms for these reactions have already been discussed in section II.2.A.c.

Conversions of $Pd(Raao)_2$ to $Pd_2(Raao)_2X_2$ have been possible in the following routes:

(i) $Pd(Raao)_2$ + $Pd(PhCN)_2X_2$ $\xrightarrow[\text{room temp.}]{\text{bz or}\ \text{EtOH}}$ $Pd_2(Raao)_2X_2$ + 2PhCN

(ii) $Pd(Raao)_2$ + PdX_2 $\xrightarrow[\text{EtOH}]{\text{boil}}$ $Pd_2(Raao)_2X_2$
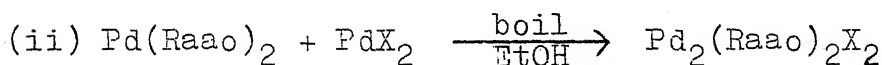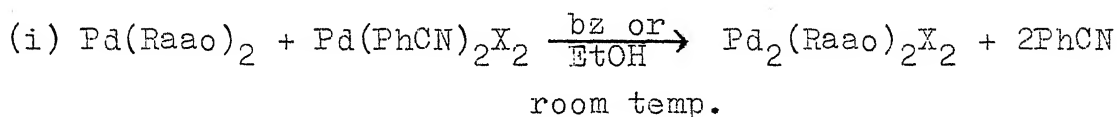
These smooth and facile interconversions clearly point out the interrelation between the two sets of complexes. Moreover, the possible syntheses of new types of complexes were attempted in view of the interconversion reactions. A few of these syntheses are discussed below.

e. Bis-arylazooximates Containing Two Different Arylazooximes

Since the conversion of $Pd_2(Raao)_2X_2$ to $Pd(Raao)_2$ involve the addition of one molecule of HRaao per Pd atom, the R group can be varied to generate species of the type $Pd(Raao)(R'aao)$ in the following reaction:

$$Pd_2(Raao)_2X_2 + 2HR'aao \xrightarrow[\substack{\text{heat with } Na_2CO_3 \\ \text{or pour into} \\ \text{water at room} \\ \text{temp. and stir}}]{\text{bz or chl}}$$

$$\cdots (10)$$
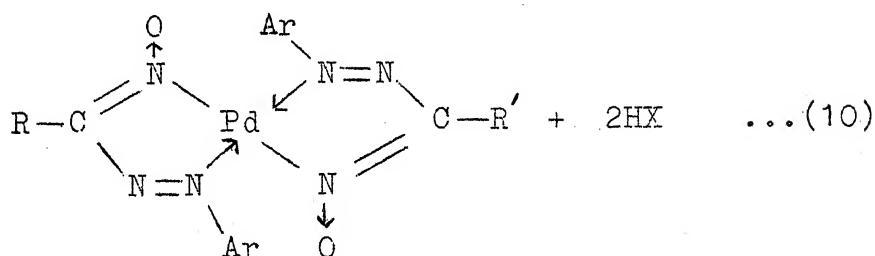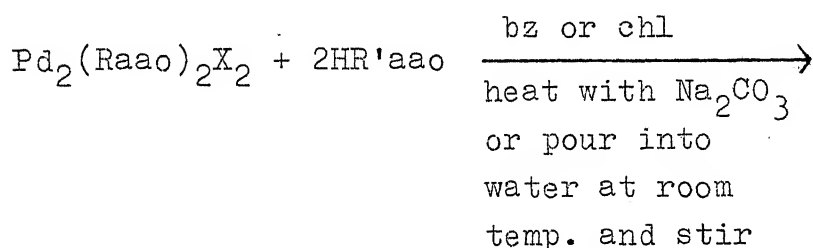
VII

The complex $Pd(Meaao)(Phaac)$ has been synthesised utilising the reaction mentioned above and has been characterised. Here also the addition of one equivalent of arylazooxime per Pd atom to $Pd_2(Raao)_2X_2$ in benzene or chloroform produces a dark brown solution which remains as such over a period of time with no further change if kept in a dry atmosphere. The presence of a base like water or Na_2CO_3 can only bring about the formation of the mixed bis-arylazooximate.

f. Palladium(II) Complex Containing One Arylazooxime Chelate and One Orthometallated Azobenzene Chelate

The observation that arylazooximes can split halogen-bridge and form chelate rings in presence of water or Na_2CO_3 encouraged us to start with different halo-bridged complexes and arylazooximes to produce mixed complexes. The first successful synthesis involves trans-μ-dichlorobis(phenylazophenyl-2C,N')dipalladium(II) (structure VIII) first reported by Cope and Siekman[2]. The addition of one equivalent of phenylazoacetaldoxime per Pd atom to VIII in benzene results in a brown solution which turns deep violet-red on heating with Na_2CO_3. The same result is obtained if the mixture of the arylazooxime and VIII in benzene is poured into water and stirred at room temperature. Addition of hexane to the concentrated violet-red benzene solution deposits bright maroon crystals of IX:

VIII

$+ 2\text{HMeaao} \xrightarrow[\substack{\text{heat with } Na_2CO_3 \\ \text{or pour into water} \\ \text{at room temp.}}]{\text{bz}}$

IX

$+ 2\text{HCl}$

...(11)
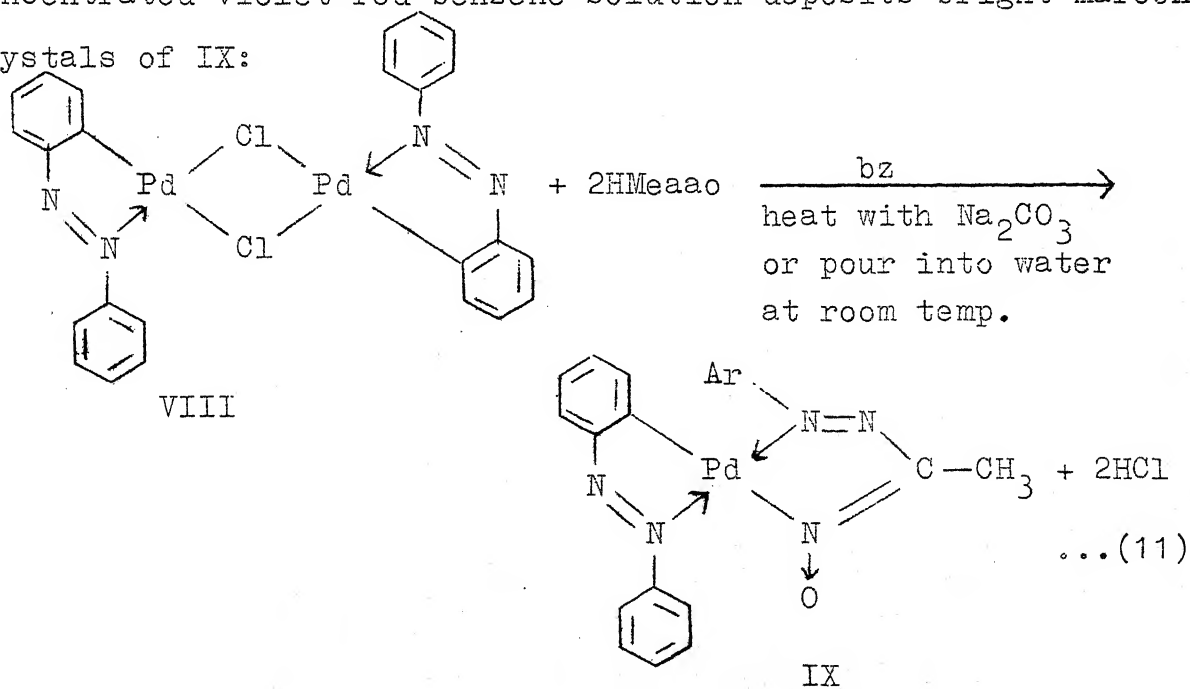
In course of this work we found a rapid and convenient synthesis of VIII. A mixture of dichlorobis(azobenzene)-palladium(II) (structure X) in chloroform and Na_2PdCl_4 in aqueous ethanol is heated to reflux for 3-4 **hrs.**   Complex VIII is produced in more than 90% yield.

$$\text{X} + Na_2PdCl_4 \xrightarrow[\text{reflux}]{\text{boil to}} \text{VIII} + 2NaCl + 2HCl \quad \dots\dots(12)$$

X
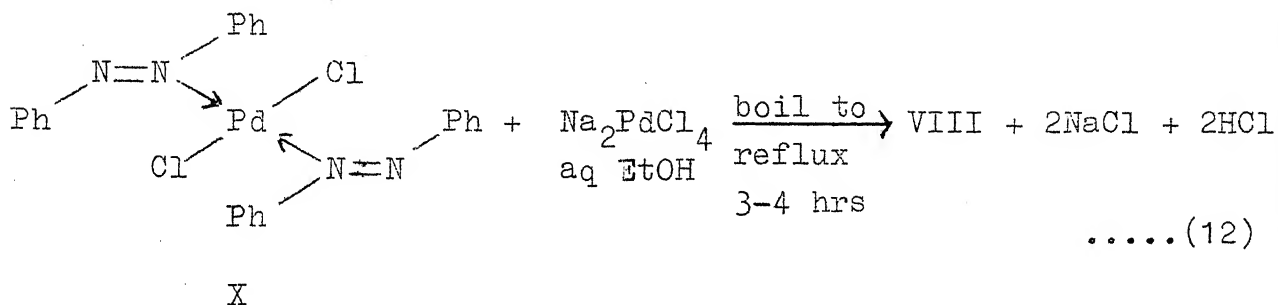
g. Attempted Synthesis of Mixed Pd(II) Complex Containing One π-allyl Chelate and One Arylazooxime Chelate

The attempt to synthesise the system XI starting from

XI
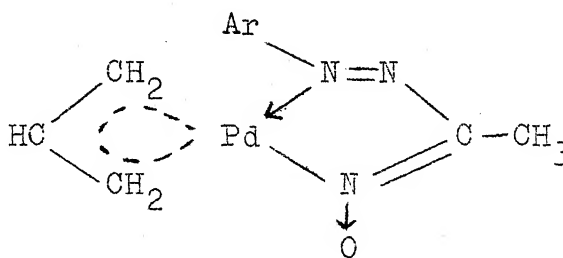
di-μ-chlorobis $\left[\pi\text{-allylpalladium(II)}\right]$ (structure XII) however, failed. The π-allyl complex reacts readily with phenyl-azoacetaldoxime (lig: Pd = 1:1) in benzene at room temperature

to produce di-μ-chlorobis$\left[\text{phenylazoacetaldoximatopalladium(II)}\right]$

HC$\overset{\text{CH}_2}{\underset{\text{CH}_2}{\big\langle}}Pd\overset{\text{Cl}}{\underset{\text{Cl}}{\big\langle\big\rangle}}Pd\overset{\text{H}_2\text{C}}{\underset{\text{H}_2\text{C}}{\big\rangle}}$CH + 2HMeaao $\longrightarrow$ I   ...(13)

XII

In this case HMeaao brings about displacement of the π-allyl group rather than splitting of the bridge.

B. Some Physical Data

a. Infrared Spectra

Infrared spectra have been of considerable use in diagonising the structure of the arylazooximates. A band of cardinal importance is ν_{N-O}. Arylazooximes in the solid state and in solution show an intense and somewhat broad band in the region 1000-1050 cm^{-1} which has been assigned to ν_{N-O} of the azooxime structure[1]. On complex formation the ν_{N-O} is shifted considerably to higher frequencies. Examples are:
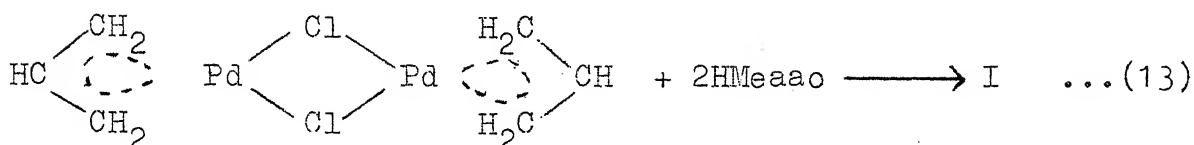
Co(Meaao)$_3$	1260 cm^{-1}	(ref. 7)
Cu(p-tolaao)$_2$	1280 cm^{-1}	(ref. 8)
NaFe(Phaao)$_3$.H$_2$O	1278 cm^{-1}	(ref. 9)
NaFe(p-tolaao)$_3$.H$_2$O	1280 cm^{-1}	(ref. 9)

The upward shift of ν_{N-O} in going from the free ligand to the complex is strongly suggestive of the binding of the

metal at oxime nitrogen (five-membered chelate ring) with consequent stabilisation of the nitrone structure XIII. This situation is of common occurance in complexes of oxime in general[10].

$$R—C\overset{\displaystyle N=N}{\underset{\displaystyle N}{\bigwedge}}\!\!\begin{matrix}Ar\\M/n\end{matrix}$$
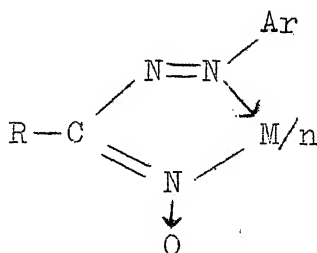
XIII

The halo-bridged and bis- arylazooximates of palladium are no exceptions. The ν_{N-O} frequencies appear in the region 1200-1300 cm^{-1} (Fig. II.1). ν_{O-H} is absent in all the cases. Representative spectra are tabulated in Table II.1, II.2 and II.3. $\nu_{N=N}$ of coordinated azo group[4] is expected in the region 1440-1600 cm^{-1}. However, the chelates show complex patterns in this region and hence $\nu_{N=N}$ could not be identified. The presence of chloro- and bromo-bridges in palladium(II) complexes is known[6,11] to give rise to medium to strong absorptions in the frequency range 300-200 cm^{-1} and 200-150 cm^{-1} respectively. The far-infrared spectra of $Pd_2(Raao)_2X_2$ where R = Me, Ph and X = Cl, Br were run. The vibrations, however, seem to be highly coupled and therefore specific assignments are quite difficult to make. The spectra are shown in Fig. II.2 and the bands tentatively assigned are shaded. In the complex $Pd_2(Meaao)_2Cl_2$, $\nu_{Pd-Cl(b)}$ appear at a slightly
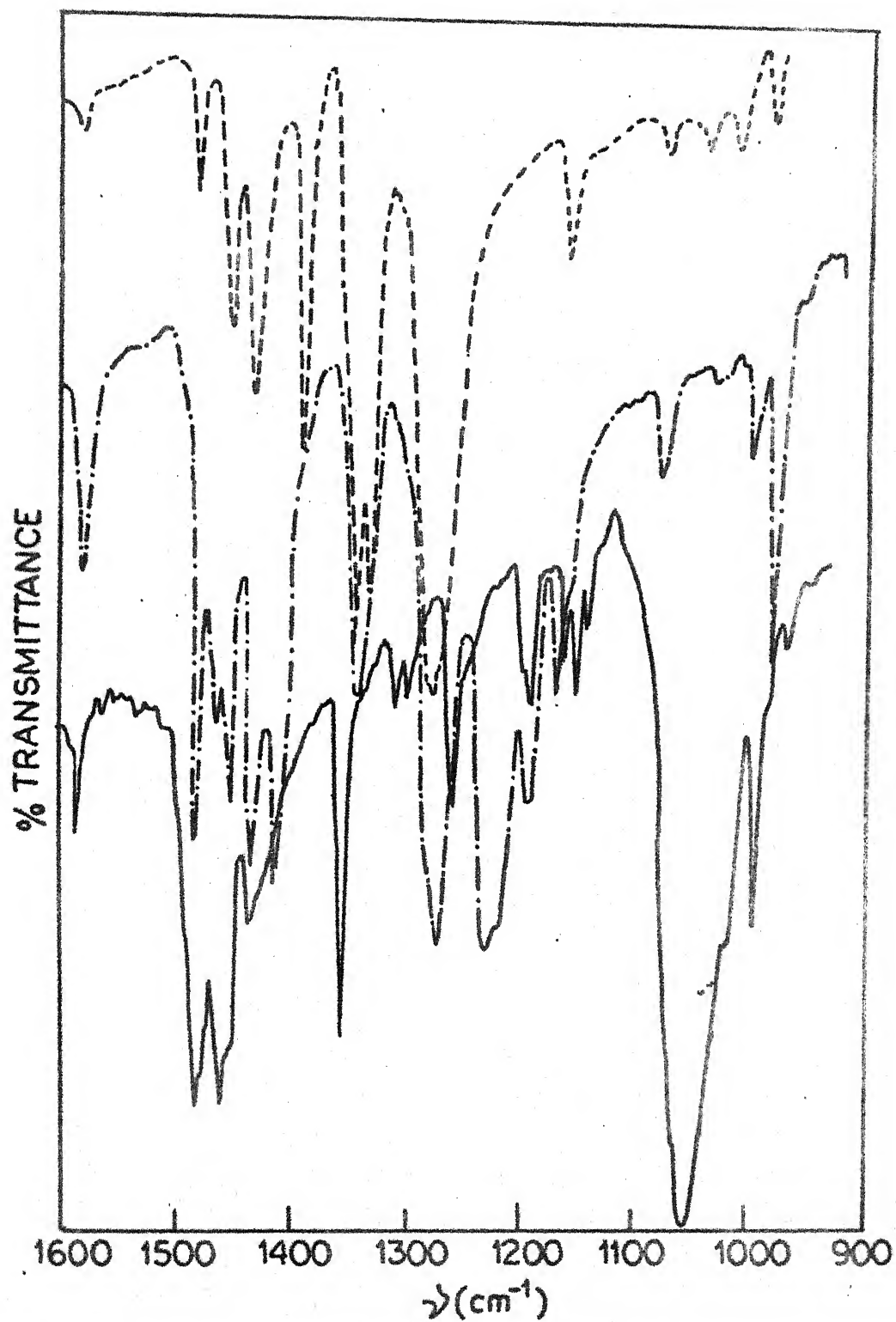
FIG II.1. PARTIAL INFRARED SPECTRA OF HMeaao(———),
Pd$_2$(Meaao)$_2$Cl$_2$(—·—·—) & Pd(Meaao)$_2$ (— — — —)
IN KBr (DISC).

TABLE II.1

INFRARED DATA OF CHLORO-BRIDGED ARYLAZOOXIMATES OF PALLADIUM(II) IN KBr DISCS (FREQUENCIES ARE IN cm^{-1}).

Compound	ν_{C-H} R	ν_{C-H} Ar	ν_{N-O}	C-H out-of-plane deformation	Other Vibrations
Pd$_2$(Meaao)$_2$Cl$_2$	2920(w)	3060(w)	1275(vs) 1230(vs)	768(s), 753(s), 690(s), 635(s), 625(s), 610(s).	1580(m),1475(s),1450(m),1425(s), 1410(m),1385(m),1350(s),1165(m), 1070(w),975(m),590(m),580(m), 510(m),450(m).
Pd$_2$(Phaao)$_2$Cl$_2$		3050(m)	1230(vs)^{a}	768(s),763(s), 743(s),695(s), 655(s),630(s), 615(m).	1590(w),1570(m),1490(m),1475(m), 1450(m),1420(s),1400(m),1365(m), 1310(w),1280(m),1200(m),1180(w), 1100(w),1070(w),525(m),450(w).
Pd$_2$(p-tolaao)$_2$Cl$_2$	2920(w)	3060(w) 3030(w)	1230(vs)^{a}	810(s),765(s), 753(s),730(m), 680(s),620(m), 610(m).	1600(w),1580(w),1560(w),1500(m), 1475(m),1450(m),1420(s),1390(s), 1365(m),1315(w),1280(m),1200(m), 1180(m),1100(m),1070(w),590(w), 510(m),485(w),470(m).

w = weak; m = medium; s = strong; vs = very strong.

a associated with three or four medium to weak absorptions.

INFRARED DATA OF BROMO-BRIDGED ARYLAZOOXIMATES OF PALLADIUM(II) IN KBr DISCS (FREQUENCIES ARE IN cm^{-1}).

Compound	ν_{C-H} R	Ar	ν_{N-O}	C-H out-of-plane deformations	Other Vibrations
$Pd_2(Meaao)_2Br_2$	2910(w)	3060(m)	1270(vs), 1215(vs)	765(s), 750(s), 693(s), 628(m), 610(m).	1570(m),1470(s),1450(s),1425(s), 1400(s),1350(s),1180(s),1160(m), 990(w),970(m),900(w),585(m), 515(m), 500(w).
$Pd_2(Phaao)_2Br_2$		3050(m).	1230(vs)[a]	765(s), 750(s), 730(m), 680(s), 645(m), 625(m), 620(m), 600(m).	1580(m),1560(w),1500(m),1480(m), 1450(m),1420(s),1385(s),1365(m), 1310(m),1200(m),1180(m),1100(m), 1070(m),1020(m),990(m),950(m), 910(m),590(m),530(s),450(m).
$Pd_2(\underline{p}-tolaao)_2Br_2$	2920(w)	3060(w) 3030(w)	1230(vs)[a]	810(s), 765(s), 750(s), 725(m), 685(s), 620(s), 610(m).	1600(w),1580(w),1560(w),1505(m), 1480(m),1450(m),1420(w),1390(s), 1365(m),1315(m),1280(m),1200(m), 1180(m),1100(m),1070(m),1015(w), 590(m),510(m),485(m),470(w).

w = weak; m = medium; s = strong; vs = very strong.

a associated with three or four medium to weak absorptions.

TABLE II.3

INFRARED DATA OF SOME ARYLAZOOXIMATES OF PALLADIUM(II)
IN KBr DISCS (FREQUENCIES ARE IN cm^{-1})

Compound	ν_{C-H} R	ν_{C-H} Ar	ν_{N-O}	C-H out-of-plane deformations	Other Vibrations
A. Bis Complexes					
Pd(Meaao)$_2$	2920(w)	3070(m)	1280(vs)	760(s),730(s), 690(s),625(s), 610(w).	1480(w),1475(m),1450(m),1425(s) 1380(s),1350(s),1330(s),1150(m), 1070(m),1000(m),900(m),535(m), 435(m).
Pd(Phaao)$_2$		3035(w) 3015(w)	1245(vs)[a]	780(s),765(s), 745(m),735(s), 707(m),692(s), 650(s),625(m), 615(s).	1600(m),1575(m),1500(m),1480(m), 1450(m),1420(s),1355(s),1315(m), 1280(m),1180(m),1150(m),1105(m), 1070(m),1020(m),1000(m),540(m), 520(m),485(m).
Pd(p-tolaao)$_2$	2920(w)	3030(m)	1245(vs)[a]	820(s),778(m), 760(s),740(s), 720(m),698(s), 645(s),630(m), 620(m),610(m).	1605(m),1560(w),1510(m),1480(m), 1460(m),1360(s),1315(m),1280(m), 1200(m),1180(m),1070(m),1015(m), 910(m),550(m),520(m),500(m), 460(m).

TABLE II.3 (contd.)

Compound	ν_{C-H} R	ν_{C-H} Ar	ν_{N-O}	C-H out-of-plane deformations	Other Vibrations
B. Mixed Species					
Pd(Meaao)(Phaao)	2920(w)	3050(m)	1265(vs) 1230(vs)	755(s),732(s), 685(s),645(m), 620(m),610(m).	1585(m),1550(m),1490(m),1480(m), 1450(s),1415(m),1385(s),1340(s), 1310(m),1200(m),1145(m),1100(m), 1065(m),990(m),910(m),560(m).
Pd(Meaao)(azbz)[b]	2920(w)	3050(m)	1150(vs)	770(s),708(m), 695(s),625(m), 620(m),610(m).	1575(s),1550(s),1500(m),1455(s), 1445(m),1390(s),1355(s),1320(m), 1305(m),1275(vs),1230(s),1195(s), 1105(m),1045(m),1020(m),910(m), 570(m),550(m),445(m).

w = weak; m = medium; s = strong; vs = very strong.

a associated with two or three medium to weak absorptions.

^ azbz = orthometallated azobenzene chelate ring.
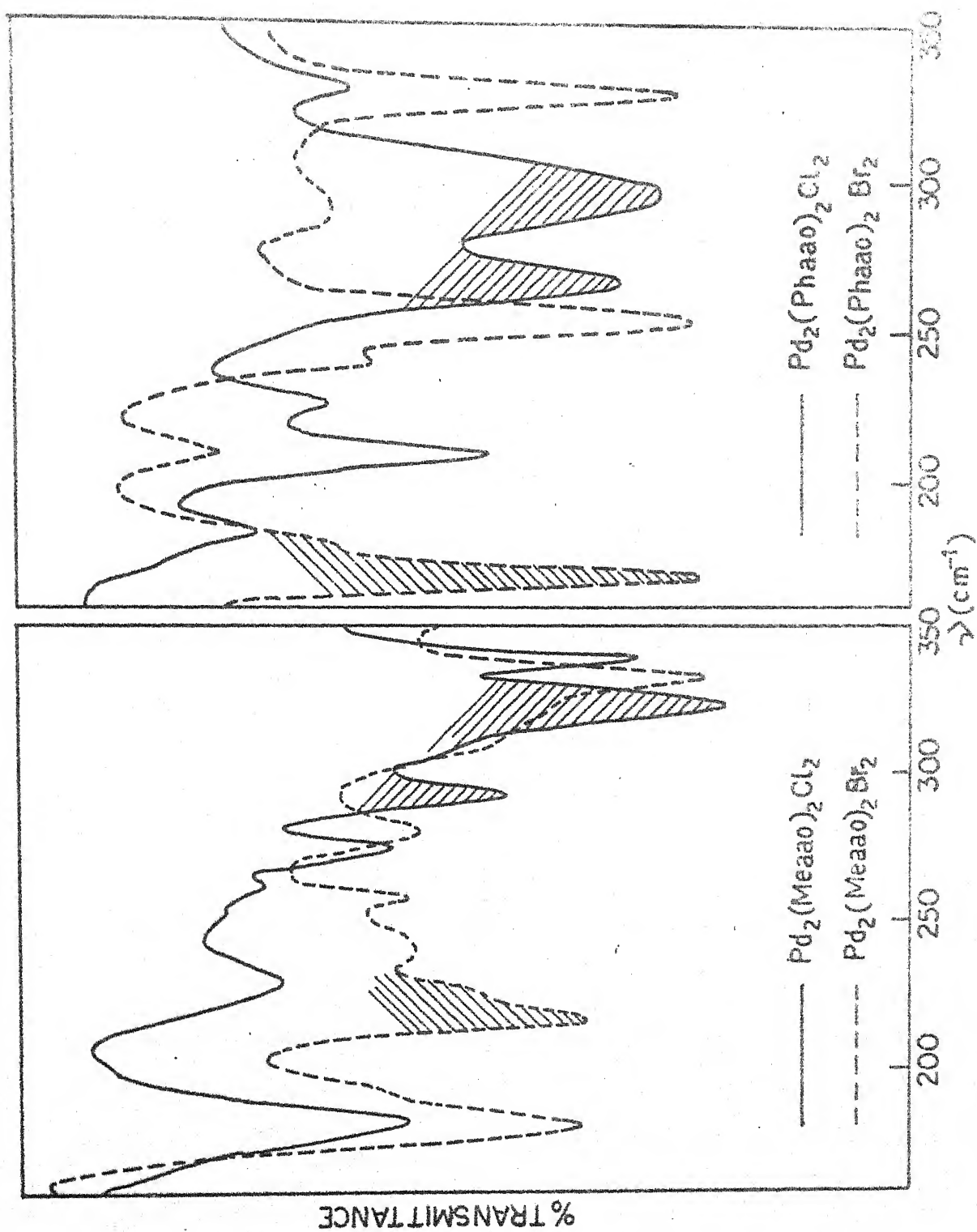
FIG II.2. FAR-INFRARED SPECTRA OF $Pd_2(Raao)_2X_2$ CHELATES IN NUJOL MULL.

Pd₂ spectrum legend:
- —— $Pd_2(Phaao)_2Cl_2$
- ---- $Pd_2(Phaao)_2Br_2$

- —— $Pd_2(Meaao)_2Cl_2$
- ---- $Pd_2(Meaao)_2Br_2$

% TRANSMITTANCE

$\gamma(cm^{-1})$

higher frequency region viz 325 cm^{-1} and 295 cm^{-1} which are, however, close to the values reported for the chloro-bridged orthometallated azobenzene complex of palladium[12].

The available results are in agreement with structures I, II and IV for the chloro-bridged, bromo-bridged and bis-arylazooximates respectively. Of these the chloro-bridged structure was discussed by us earlier[1]. The bis-complexes can exist in cis- and trans- form. Only one type of crystalline solid can however, be isolated in each case. Chromatography on a column of allumina fails to show the presence of more than one separable species. The cis- formulation of the bis-complexes seems unlikely because of steric crowding of the phenyl rings. We propose the trans- structure for IV.

The ν_{N-O} in the mixed bis-arylazooximate Pd(Meaao)(Phaao) appears as a double-humped strong band with maxima at 1265 cm^{-1} and 1230 cm^{-1} (Fig. II.3.a). The other mixed complex IX exhibits a very strong and somewhat broad band around 1150 cm^{-1} which could most possibly be the ν_{N-O} (Fig.II.3b).

b. Electronic Spectra

Electronic spectral data for the halo-bridged arylazooximates are collected in Table II.4 and two typical spectra are illustrated in Fig. II.4. The halo-bridged complexes invariably show an intense band at ~550 nm (complexes of HMeaao have another intense band around 380 nm) with an

% TRANSMITTANCE

Pd(Meaao)₂
Pd(Phaao)₂
Pd(Meaao)(Phaao)

(a)

(b)

ν_{NO}

ν(cm⁻¹)
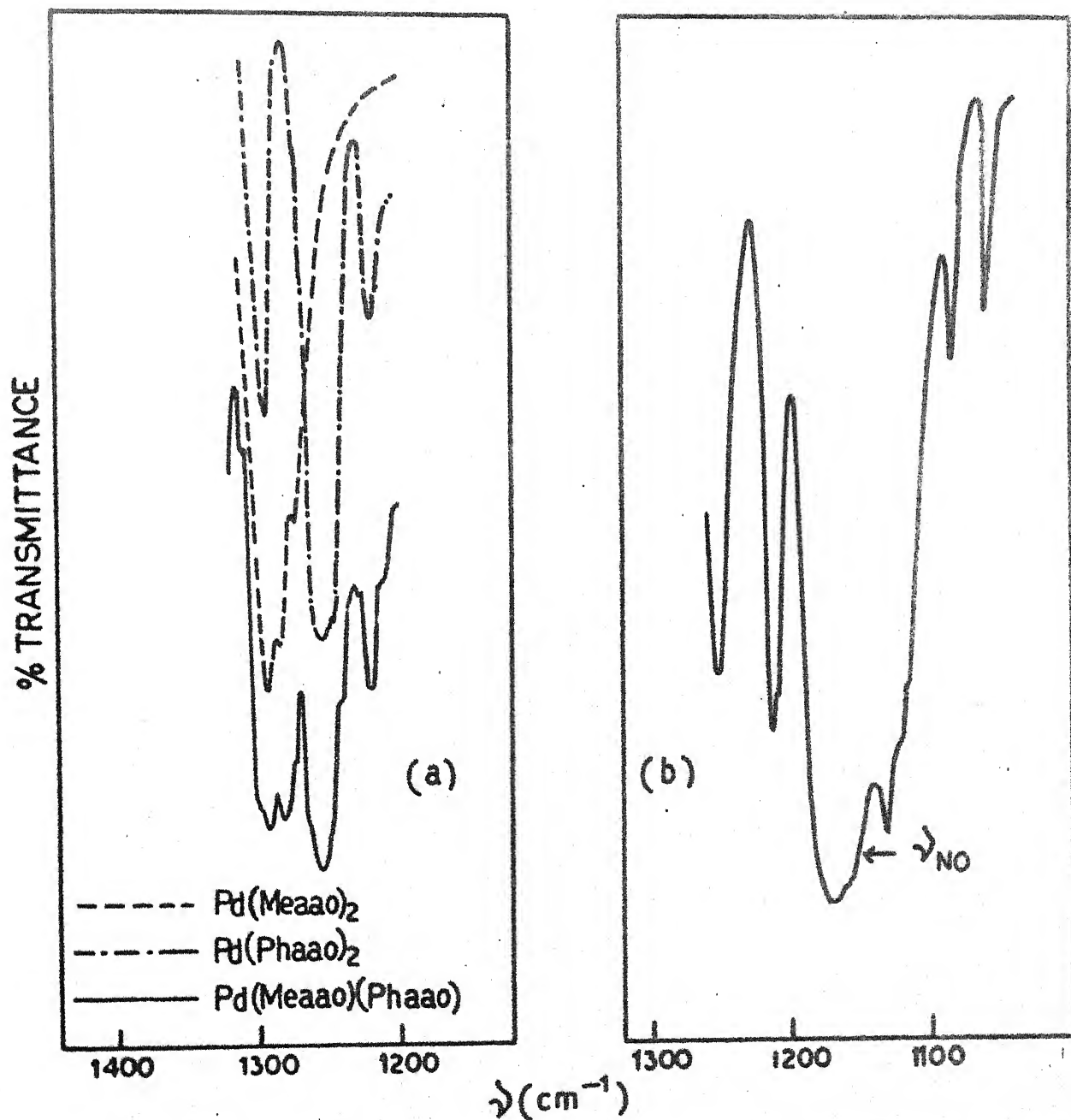
FIG Ⅱ.3 PARTIAL INFRARED SPECTRA (THE ν_{NO} REGION) OF (a) Pd(Meaao)(Phaao) AND (b) Pd(Meaao)(azbz) IN KBr(DISC).

TABLE II.4

ELECTRONIC SPECTRAL DATA OF THE HALO-BRIDGED ARYLAZOOXIMATES OF PALLADIUM(II) IN BENZENE AT ROOM TEMPERATURES (λ = BAND MAXIMUM IN nm; ϵ = EXTINCTION COEFFICIENT IN $M^{-1}cm^{-1}$).

Compound	λ (ϵ)
$Pd_2(Meaao)_2Cl_2$ [a]	535 (10,200), 370 (14,300)
$Pd_2(Phaac)_2Cl_2$ [b]	545 –
$Pd_2(Meaao)_2Br_2$	545 (10,600), 380 (17,000)

a In chloroform, the peak positions are at 530 nm and 370 nm.

b Only qualitative spectrum was run because the compound is very sparingly soluble.

FIG II.4. ELECTRONIC SPECTRA OF TWO HALO-BRIDGED ARYLAZOOXIMATES OF PALLADIUM(II) IN BENZENE.

extinction coefficient of $\sim$ 5000 per Pd atom. As R changes
from Me to Ph, a small red shift is observed (Table II.4).
A small red shift is also noted when the bridging X changes
from Cl to Br (Table II.4). The extinction coefficient of
$\sim$ 5000 per Pd atom appears to be characteristic of the chelate
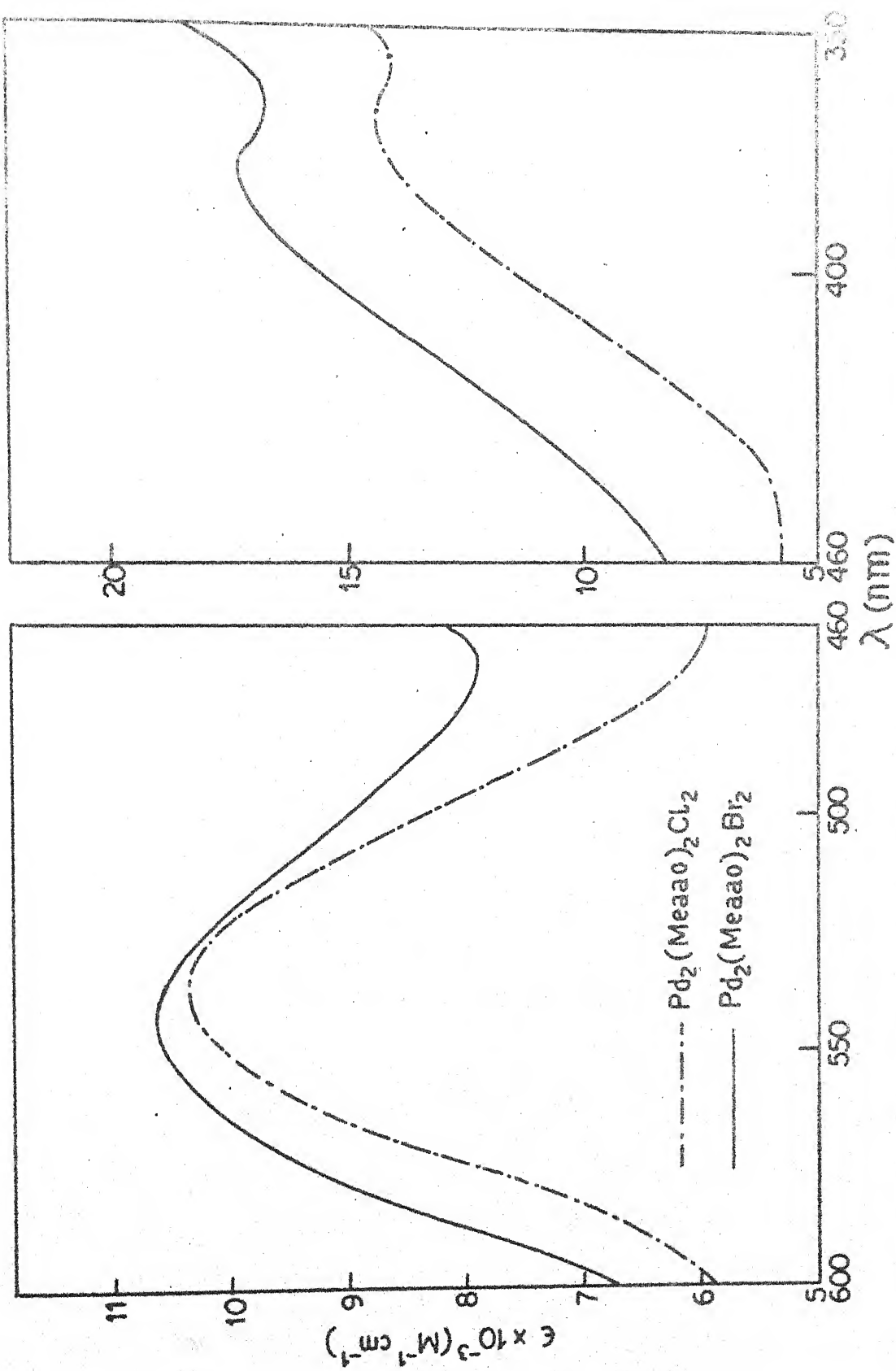moiety XIII which is present not only in the halo-bridged
complexes but also in the bridge-split products of the
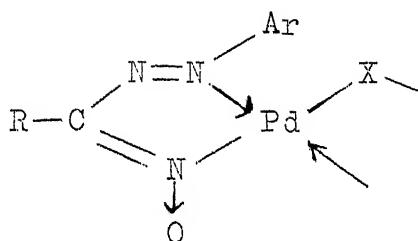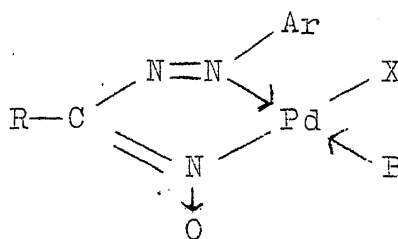
XIII   XIV

type XIV (Chapter III). When the arylazooxime chelate ring
is opened either at the azo-end or at the oxime-end the band
at $\sim$ 550 nm disappears (Chapter IV). Although we have not
established the origin of this band, it appears to be a
metal $\longrightarrow$ ligand (M $\longrightarrow$ L) charge transfer transition.
In the mixed complex IX, where again the moiety XIII is present,
we get a band at 560 nm with an extinction coefficient of
6000.

In the bis-arylazooximates, an intense band with a
double-humped structure appears at a relatively lower energy
region ($\sim$ 630 nm). A typical spectrum is shown in Fig.II.5
and the electronic spectral data are presented in Table II.5.
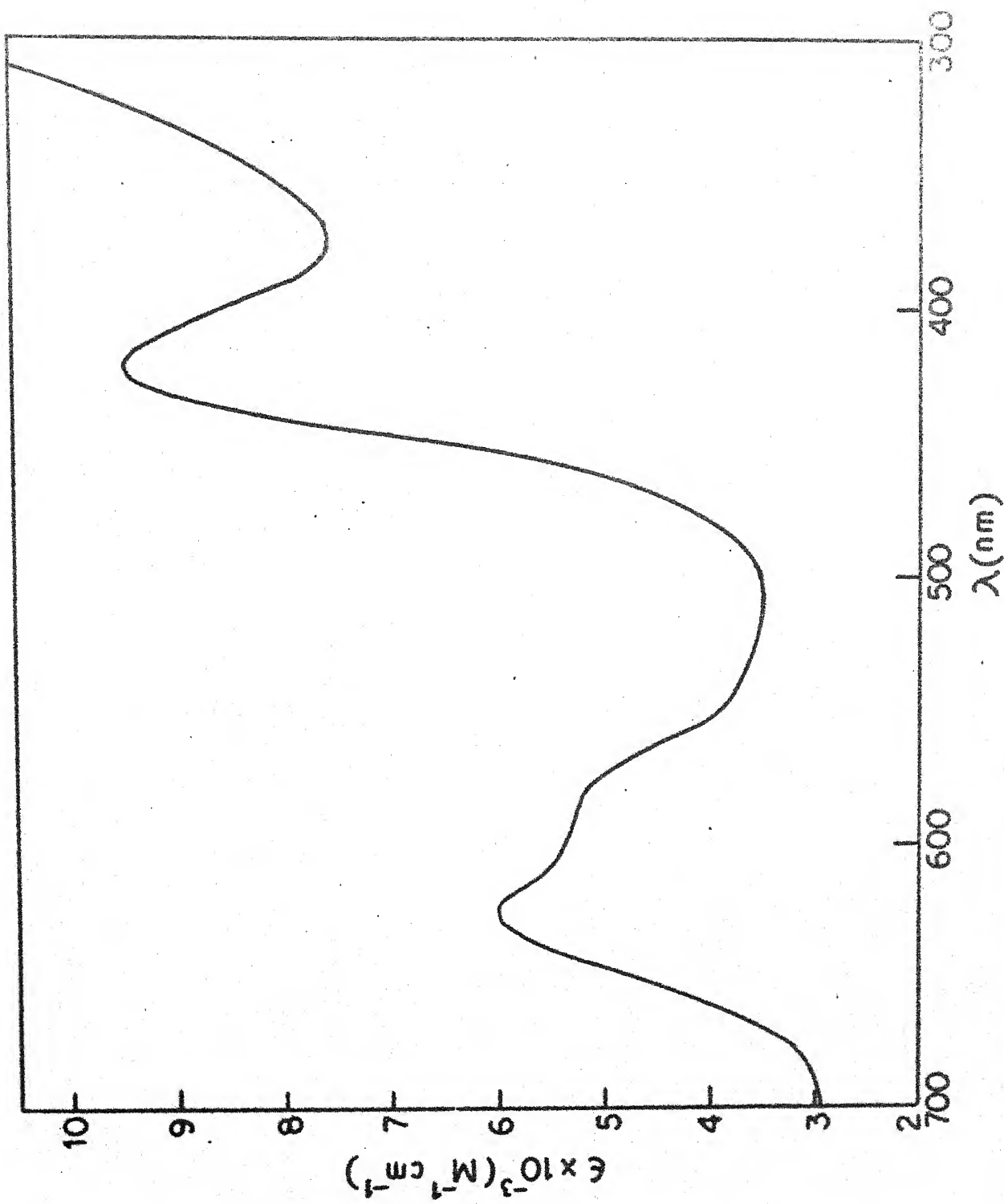
FIG II.5. ELECTRONIC SPECTRUM OF BIS(PHENYLAZOACETALDOXIMATO)-
PALLADIUM(II) IN BENZENE.

TABLE

ELECTROₙIC SPECTRAL DATA OF THE BIS–ARYLAZOOXIMATES AND OTHER MIXED
COMPLEXES OF PALLADIUM(II) IN BENZENE AT ROOM TEMPERATURE (λ= BAND
MAXIMUM IN nm; ϵ = EXTINCTION COEFFICIENT IN $M^{-1}cm^{-1}$).

Compound	λ (ϵ)
Pd(Meaao)$_2$[a]	625(6,000), 585 sh[d](5,250), 420 (9,400)
Pd(Phaao)$_2$[b]	635(6,000), 600 sh (5,350), 435(10,000)
Pd(p–tolaao)$_2$[c]	645(5,800), 605 sh (4,950), 445 (9,000)
Pd(Meaao)(Phaao)	630(5,000), 590 sh (4,200), 430 (7,650)
Pd(Meaao)(azbz)	560(6,000), 450 sh (5,850), 410 sh (8,660)

In chloroform, the peak positions are [a] 615, 580 sh and 410 nm; [b] 630, 585 sh and 425 nm;
[c] 635, 600 sh and 430 nm; [d] sh stands for shoulder.

The extinction coefficient of this band lies in the range 4500-6000. The bis-complexes have in general another band around ∼420 nm with extinction coefficient of about 10,000. All the bands of the bis-complexes show a solvent shift of 10 to 15 nm to the higher energy side when the solvent is changed from benzene to chloroform. Attempts to locate crystal field bands failed because of the presence of intense charge transfer bands in the visible region.

c. Proton Magnetic Resonance Spectra

The pmr spectra of the halo-bridged complexes could not be run because they are sparingly soluble in chloroform, benzene and other organic solvents. Among the bis-arylazooximates, only the complex $Pd(Meaao)_2$ is sufficiently soluble in chloroform and its pmr spectrum at room temperature is shown in Fig.II.6. The spectrum is consistent with the structure IV (R = Me). The room temperature pmr spectrum of Pd(Meaao)(azbz) in $CDCl_3$ is also displayed in Fig. II.6.

II.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Starting Compounds

(i) Palladium(II) bromide:

A solution of 1.84 gm of potassium tetrachloro-palladate(II) was prepared by heating 1 gm of palladium(II)
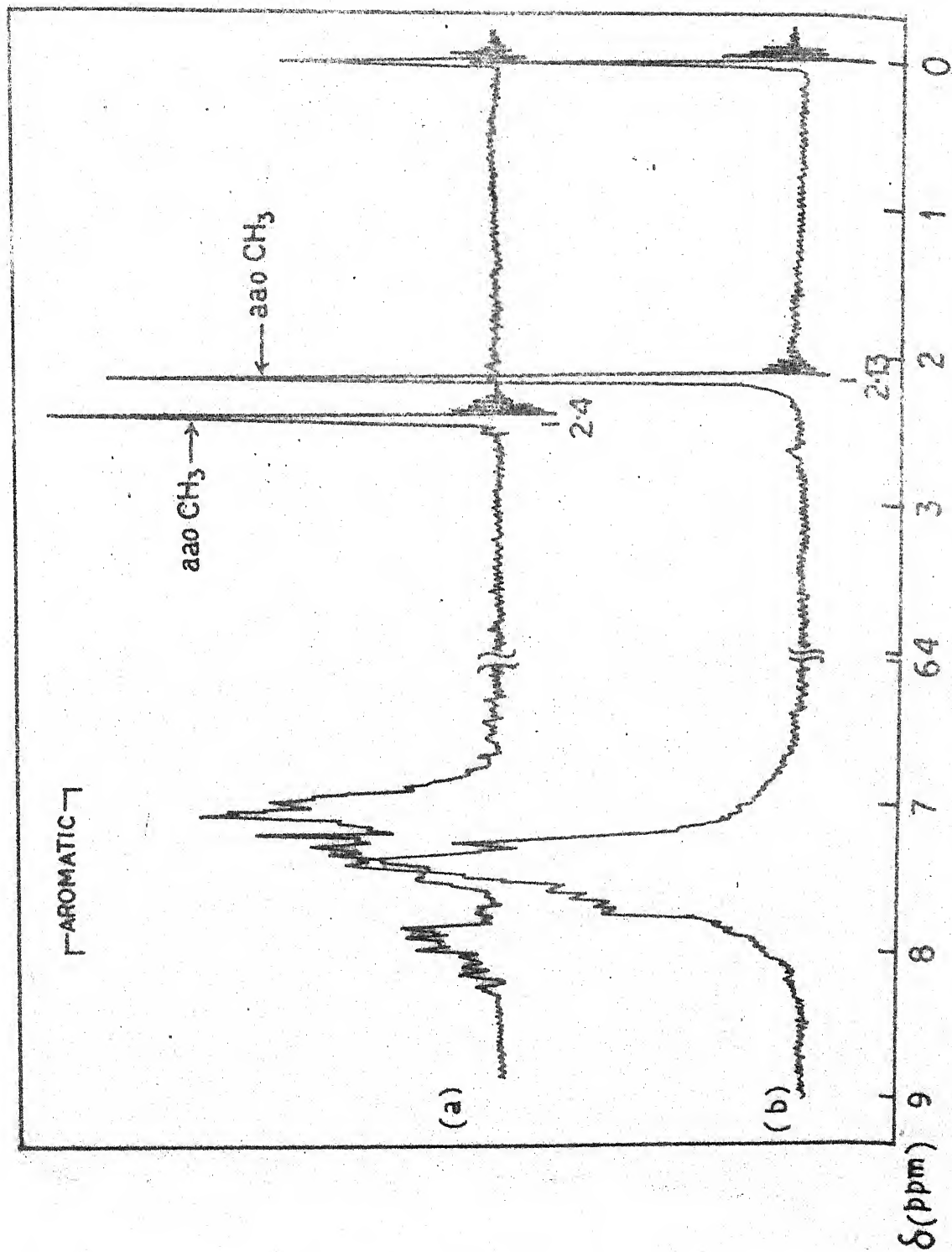
FIG II.6. PMR SPECTRA OF (a) BIS (PHENYLAZOACETALDOXIMATO) PALLADIUM(II) AND (b)(PHENYLAZOACETALDOXIMATO) (PHENYLAZOPHENYL—2 C,N) PALLADIUM (II)

chloride (Johnson Matthey Chemicals Ltd., London) and 840 mg
of A.R. potassium chloride (Sarabhai Merck Ltd., India) in
25 ml of distilled water. To this hot solution of K_2PdCl_4,
hydrazine hydrochloride (E.Merck, Germany) was slowly added
in small batches (total $\sim$ 3 gms). The solution turned dark and
deposition of metallic palladium started. After the addition
of the total amount of hydrazine hydrochloride, the solution
was left for 15 minutes when the precipitated palladium coagu-
lated to an ash colored mass. It was then filtered, washed with
water and then redissolved in $\sim$ 8 ml of hot A.R hydrobromic acid
(plus 4 drops of conc nitric acid). The metal dissolved
smoothly on heating to give a dark red solution which was then
carefully and slowly evaporated (on hot plate) to 0.2 ml.
Again 2 ml of HBr was added and the solution was evaporated
slowly to a dark brown slurry. The slurry was then kept in
vacuum over KOH beads for 24 hours when dark brown powder of
$PdBr_2$ was left.

(ii) Bis(benzonitrile) Complexes $Pd(PhCN)_2X_2$ where
X = Cl or Br [3,13]:

Palladium(II) halide (1 gm of either $PdCl_2$ or $PdBr_2$) was
suspended in 25 ml of benzonitrile (E. Merck, Germany) and the
mixture was heated to $100^{\circ}C$ (on water bath) for 20 minutes by
which time the majority of the palladium(II) halide dissolved to
give a deep red solution. The solution was then filtered while
still warm and the filtrate was poured into low boiling light
roleum (200 ml) when light yellow precipitate appeared. The

precipitate was filtered off, washed with light petroleum and dried to obtain about 95% yield of $Pd(PhCN)_2X_2$.

b. Ligands

(i) Chemicals

Aldehydes: Acetaldehyde was prepared by distilling paraaldehyde with a few drops of concentrated H_2SO_4 and collecting the aldehyde in an ice-cooled receiver.

Benzaldehyde was obtained from Albright & Wilson Mfg. Co. Ltd., England, and was used straight from bottles. p-tolualdehyde was procured from Aldrich Chemical Co.,U.S.A., and was used as such.

n-Butylnitrite was prepared by reacting n-butyl alcohol with nitrous acid.

(ii) Arylazooximes

These were prepared by Bamberger[14] by carrying out the nitrosation of arylhydrazones of aldehydes using amylnitrite. Later these were prepared in this laboratory[15] using n-butyl-nitrite instead of amylnitrite. Arylazooximes for this work was prepared using the latter method with a few changes so as to get better yields.

Preparation of Phenylhydrazones of Aldehydes

Phenylhydrazones of benzaldehyde and p-tolualdehyde were prepared by shaking the aldehydes with phenylhydrazine (1:1 molar ratio) in acetic acid. The uniform pale yellow solids were filtered, washed with dilute acetic acid and aqueous ethanol and finally dried in hot air oven at $60^{o}C$.

Acetaldehydephenylhydrazone was prepared according to the procedure of Bamberger[14] with a little modification. The reaction was carried out at $0^{o}C$ rather than $10^{o}C$ so as to obtain shinning crystals of the hydrazone in better yield.

Arylazooximes from the Phenylhydrazones

Arylazooximes with R= alkyl were prepared as follows:
0.03 mol of phenylhydrazone was dissolved in 30 ml of ether. 0.2 mol of butylnitrite was added to the above solution and was kept for 4 hrs at room temperature. The reaction mixture which turned deep reddish brown was extracted with 3 x 35 ml portions of 0.5 N sodium hydroxide. The aqueous extract was cooled to $0^{o}C$ and then neutralised by drop-wise addition of cold 1N sulphuric acid. During this process the color of the solution became progressively lighter and towards the end arylazooxime started separating out as an orange crystalline precipitate. Care was taken so that the temperature during the neutralisation step did not rise above $0^{o}C$. The orange solid was filtered, washed with water, dried and

recrystallised from hexane-dichloromethane mixture.
Arylazooximes with R = aryl were prepared as described below:

0.1 mol of phenylhydrazone was dissolved in 150 ml of methanol (A.R grade). 0.2 mol of butylnitrite was added to it followed by 0.15 mol of potassium tertiary butoxide (or 0.2 mol of sodium methoxide). Immediately a red coloration developed. The mixture was heated to reflux for 1 hr, then cooled to room temperature and filtered. To the filtrate was added 0.2 mol of NaOH in 300 ml of water. The mixture was kept overnight in the refrigerator and then extracted with ether. The aqueous layer was cooled to 0°C and neutralised with 1N sulphuric acid maintaining the temperature at 0°C. The yellow solid which separated out was filtered, washed with water, dried and recrystallised from hexane-dichloromethane mixture.

c. Halo-bridged Arylazooximates

(i) From K_2PdX_4

The preparations of the chloro-bridged arylazooximates of palladium(II) from aqueous K_2PdCl_4 and alcoholic arylazo-oximes are already described in ref. 1. One representative preparation of bromo-bridged palladium(II) complex is given below.

Di-μ-bromobis [phenylazoacetaldoximatopalladium(II)],
Compound II (R = CH$_3$)

To a solution of 168 mg (0.3 mmol) of K$_2$PdBr$_4$ in 10 ml of water was added drop-wise and with constant stirring, a solution of 55 mg (0.3 mmol) of phenylazoacetaldoxime in 5 ml of ethanol. Immediately the solution turned violet and crystals started separating out. Recrystallisation from ethanol resulted in 100 mg of pure product.

(ii) From Pd(PhCN)$_2$X$_2$

Di-μ-chlorobis [phenylazobenzaldoximatopalladium(II)],
Compound I (R = C$_6$H$_5$)

384 mg (1 mmol) of Pd(PhCN)$_2$Cl$_2$ was dissolved in 25 cc of dehydrated ethanol and to it was added, slowly with stirring, a solution of 225 mg (1 mmol) of phenylazobenzaldoxime in 15 ml of dehydrated ethanol. The solution immediately turned purple and purple crystals started depositing. After the addition of the ligand was complete, the mixture was stirred for another 15 minutes and then the crystals were filtered, washed thoroughly with dehydrated ethanol and dried over fused CaCl$_2$. The yield was $\sim$ 90%.

The complexes di-μ-chlorobis [phenylazoacetaldoximato-palladium(II)] and di-μ-chlorobis [phenylazo-p-tolualdoximato-palladium(II)] were prepared by similar procedures.

Use of benzene in place of dehydrated ethanol as solvent in the above syntheses produced similar yields.

Di-μ-bromobis$\left[\text{phenylazo-}\underline{\text{p}}\text{-tolualdoximatopalladium(II)}\right]$,

Compound II (R = $C_6H_4CH_3(\underline{\text{p}})$)

236 mg (0.5 mmol) of $Pd(PhCN)_2Br_2$ was dissolved in 25 ml of dehydrated ethanol and the solution was heated to $60^\circ C$. To this hot solution was added, dropwise with stirring a solution of 120 mg (0.5 mmol) of phenylazo-$\underline{\text{p}}$-tolualdoxime in 20 ml of dehydrated ethanol. The solution turned violet and then purple and purple solid separated. After 30 minutes of stirring, the purple crystalline solid was filtered, washed thoroughly with dehydrated ethanol and dried over fused $CaCl_2$. The yield was $\sim$92%.

The syntheses of di-μ-bromobis$\left[\text{phenylazoacetaldoximatopalladium(II)}\right]$ and di-μ-bromobis$\left[\text{phenylazobenzaldoximatopalladium(II)}\right]$follow similar procedures.

Reaction of $Pd(PhCN)_2Br_2$ with phenylazo-$\underline{\text{p}}$-tolualdoxime(molar ratio 1:1) in Benzene

142 mg (0.3 mmol) of $Pd(PhCN)_2Br_2$ was dissolved in 20 ml of benzene and to it a solution of 72 mg (0.3 mmol) of phenylazo-$\underline{\text{p}}$-tolualdoxime in 10 ml of benzene was added slowly with stirring. The color of the solution turned brown and slowly

deep red crystalline precipitate of III (section II.2.A.b) deposited. No further change was observed even after 1 hr of constant stirring at room temperature.

Next, 3 ml of rectified spirit was added to the above mixture when the red precipitate sharply turned purple. The mixture was further stirred for 10 minutes and then the purple precipitate was filtered, washed thoroughly first with benzene and then with dehydrated ethanol and finally dried over fused $CaCl_2$. The yield of di-μ-bromobis[phenylazo-p-tolualdoximatopalladium(II)] was ∼ 90%.

Conversion of the red crystalline precipitate of III to di-μ-bromobis[phenylazo-p-tolualdoximatopalladium(II)] was also brought about by keeping the red crystals of III in contact with moist air. The conversion is however, quite slow.

Similar observations were noted in the 1:1 reaction of $Pd(PhCN)_2Br_2$ with phenylazobenzaldoxime in benzene.

(iii) <u>From PdX$_2$</u>

<u>Di-μ-chlorobis[phenylazoacetaldoximatopalladium(II)]</u>, <u>Compound I (R = CH$_3$)</u>

177 mg (1 mmol) of $PdCl_2$ was added to a solution of 163 mg (1 mmol) of phenylazoacetaldoxime in 20 ml of dehydrated ethanol. Immediately a violet color developed. The mixture was then boiled to reflux for 1 hr. It was subsequently cooled

and the shinning violet needle-shaped crystals were filtered, washed with ethanol and dried over fused $CaCl_2$ (yield $\sim 85\%$).

Di-μ-chlorobis $\left[\text{phenylazobenzaldoximatopalladium(II)}\right]$ and di-μ-chlorobis $\left[\text{phenylazo-}\underline{p}\text{-tolualdoximatopalladium(II)}\right]$ were prepared in analogous ways.

The corresponding bromo-bridged complexes were synthesised from $PdBr_2$ by similar procedure.

(iv) From Bis(arylazooximato)palladium(II) and Halogens

Halogens

Dichlorine was generated by adding concentrated A.R hydrochloric acid to potassium permanganate (E. Merck, Germany) and passing the gas through a water-trap to remove trace of hydrogen chloride. Dibromine was procured from Reidel Co. (Germany).

Di-μ-chlorobis $\left[\text{phenylazoacetaldoximatopalladium(II)}\right]$ from Bis(phenylazoacetaldoximato)palladium(II) and Dichlorine

250 mg of bis(phenylazoacetaldoximato)palladium(II) was dissolved in 15 ml of benzene and the green solution was very carefully exposed to dichlorine for ~ 10 seconds with constant stirring. The green color turned sharply to deep red. The exposure time was carefully controlled so that no precipitation occured. The CLEAR RED solution was then slowly evaporated

(on hot plate) to 2 ml and 5 ml of dehydrated ethanol was added to it when violet needles of di-μ-chlorobis[phenylazo-acetaldoximatopalladium(II)] were deposited. The crystals were filtered, washed with 10 ml of dehydrated ethanol and dried over fused $CaCl_2$ (yield $\sim$ 80%).

With excess dichlorine the situation was quite complicated. As a few bubbles of dichlorine were passed through the benzene solution, the red color faded and a dark gummy precipitate was deposited. Brown scum accumulated on the sides of the beaker. The dark gummy precipitate turned to a brown solid in contact with air and it was found to contain $PdCl_2$ together with some organic compounds. No attempt was made to identify these organic compounds.

Di-μ-chlorobis[phenylazobenzaldoximatopalladium(II)] from Bis(phenylazobenzaldoximato)palladium(II) and Dichlorine

150 mg of bis(phenylazobenzaldoximato)palladium(II) was taken in 25 ml of benzene and was heated to get a clear green solution. The solution was then cooled to room temperature and was carefully exposed (with constant stirring) to dichlorine for $\sim$ 15 seconds when the green color turned sharply to red. Care was taken so that no brown scum or precipitate appeared at this stage due to excess dichlorine. The deep red solution was then slowly heated on hot plate when purple solid started separating out from the red solution. After 2 minutes of

heating the mixture was allowed to cool and to this 5 ml of ethanol was added. The purple solid was filtered, washed thoroughly with ethanol and finally dried over fused $CaCl_2$ (yield $\sim$ 85%).

Observations with excess dichlorine are similar to those mentioned above.

Di-μ-bromobis[phenylazoacetaldoximatopalladium(II)] from Bis(phenylazoacetaldoximato)palladium(II) and Dibromine

215 mg (0.5 mmol) of bis(phenylazoacetaldoximato)palladium(II) was dissolved in 20 ml of benzene and to it was added slowly with constant stirring a solution of 80 mg (0.5 mmol) of dibromine in 2 ml of benzene. The green solution turned reddish brown but no precipitation or turbidity was observed. The clear reddish brown solution was then allowed to evaporate slowly on hot plate. When the volume of the solution was $\sim$3 ml, it was cooled and 10 ml of dehydrated ethanol was added to it when violet needles of di-μ-bromobis[phenylazoacetaldoximato-palladium(II)] were deposited. The crystals were filtered, washed with ethanol and finally dried over fused $CaCl_2$ (yield $\sim$ 80%).

When bis(phenylazoacetaldoximato)palladium(II) was allowed to react with excess dibromine (with 3.5 times Br_2 or more), a turbid brown solution with a little dark gummy

precipitate was obtained. The gummy precipitate was found to contain $PdBr_2$ along with some organic compounds. The reaction was not investigated further.

Di-μ-bromobis[phenylazobenzaldoximatopalladium(II)] was obtained from the 1:1 reaction between bis(phenylazobenzaldoximato)palladium(II) and dibromine in an analogous manner.

d. Bis-arylazooximates

(i) From K_2PdCl_4

Bis(phenylazoacetaldoximato)palladium(II)

To a solution of 326 mg (1 mmol) of K_2PdCl_4 in 30 ml of water was added, VERY SLOWLY, dropwise and with constant stirring a solution of 570 mg (3.5 mmol) of phenylazoacetaldoxime in 15 ml of ethanol. During the initial part of the addition of the ligand a violet precipitate appeared which slowly turned black as the addition continued. After the addition was complete (which took about 20 minutes) the mixture was further stirred for 15 minutes and then the precipitate was filtered, washed thoroughly with water and dried. The dark solid was finally recrystallised from benzene-hexane mixture (yield $\sim$ 75%).

Bis(phenylazobenzaldoximato)palladium(II)

326 mg (1 mmol) of K_2PdCl_4 was dissolved in 30 ml of water and to it was added, slowly with constant stirring a

solution of 450 mg (2 mmol) of phenylazobenzaldoxime in 15 ml
of ethanol. Immediately the solution turned dark and dark green
precipitate came down. After the addition of the ligand was
complete, the mixture was stirred for 15 minutes and the
precipitate was collected by filtration, washed with aqueous
ethanol and dried. The dark green solid thus obtained was
dissolved in benzene and the resulting green solution was slowly
concentrated (on hot plate). Later, 10 ml of hexane was added
when shinning dark needles were deposited. The crystals were
collected by filtration, washed with little benzene and finally
dried in air (yield $\sim$ 85%).

Bis(phenylazo-p-tolualdoximato)palladium(II) was
prepared by a similar procedure.

(ii) From $Pd(PhCN)_2Cl_2$:

Bis(phenylazo-p-tolualdoximato)palladium(II)

To a solution of 383.5 mg (1 mmol) of $Pd(PhCN)_2Cl_2$
in 30 ml of 95% ethanol was added slowly with stirring a solution
of 478.2 mg (2 mmol) of phenylazo-p-tolualdoxime in 15 ml of
ethanol. The purple solid separated during the initial part of
the addition of the ligand turned dark as the addition continued.
After the addition of the ligand was complete the stirring was
further continued for 15 minutes. The precipitate was then
collected by filtration, washed with aqueous ethanol and dried.

It was finally recrystallised from benzene-hexane mixture. The yield of the dark shinning crystalline solid was ∿ 80%.

Bis(phenylazobenzaldoximato)palladium(II) was synthesised similarly.

(iii) From $Pd_2(Raao)_2X_2$

Bis(phenylazoacetaldoximato)palladium(II) from Di-μ-chlorobis[phenylazoacetaldoximatopalladium(II)] and phenylazoacetaldoxime

Method 1. A solution of 182.4 mg (0.3 mmol) of di-μ-chlorobis-[phenylazoacetaldoximatopalladium(II)] in 30 ml of benzene (violet in color) was mixed with a solution of 98 mg (0.6 mmol) of phenylazoacetaldoxime in 10 ml of benzene and the resulting reddish-brown solution was poured into 25 ml of water and stirred. The benzene layer turned deep green. The benzene layer was then separated from the aqueous layer and slowly concentrated (on hot plate) to ∿ 5 ml. 10 ml of hexane was added to it when dark shinning crystals of bis(phenylazoacetal-doximato)palladium(II) separated. The crystals were collected by filtration, washed with hexane and dried in air (yield ∿ 65%).

Method 2. A solution of 182.4 mg (0.3 mmol) of di-μ-chlorobis-[phenylazoacetaldoximatopalladium(II)] in 30 ml of benzene was mixed with a solution of 98 mg (0.6 mmol) of phenylazoacetaldoxime

in 10 ml of benzene and the resulting reddish brown solution
was heated to boiling (5 minutes) with 2 gms of anhydrous
sodium carbonate (G.R grade). The color of the benzene solution
turned deep green. It was then filtered and the deep green
filtrate was slowly concentrated (on hot plate) to ∼ 5 ml.
10 ml of hexane was added to it when dark shinning crystals
of bis(phenylazoacetaldoximato)palladium(II) were deposited.
The crystals were collected by filtration, washed with hexane
and dried in air (yield ∼ 70%).

Bis(phenylazoacetaldoximato)palladium(II) can be
prepared from di-μ-bromobis[phenylazoacetaldoximatopalladium(II)]
and phenylazoacetaldoxime (molar ratio 1:2) following either of
the two methods described above.

The syntheses of bis(phenylazobenzaldoximato)palladium(II)
and bis(phenylazo-p-tolualdoximato)palladium(II) from the res-
pective halo-bridged arylazooximate and arylazooxime (molar
ratio 1:2) follow similar procedures. The yields in all these
cases are higher than 80%.

e. Mixed Species

(i) Bis-arylazooximates Containing Two Different
   Arylazooximes Pd(Meaao)(Phaao) :

Method 1. A solution of 182.4 mg (0.3 mmol) of di-μ-chlorobis-
[phenylazoacetaldoximatopalladium(II)] in 30 ml of benzene was

mixed with a solution of 135 mg (0.6 mmol) of phenylazobenzaldo-
xime in 10 ml of benzene and the reddish brown solution thus
resulted was poured into 25 ml of water and stirred. The color
of the benzene layer was changed to deep green. The organic
layer was then separated from the aqueous layer and concentrated
(on hot plate) to ∿ 5 ml. 10 ml of hexane was added to it when
dark shinning crystals of (phenylazoacetaldoximato)(phenylazo-
benzaldoximato)palladium(II) separated. The crystals were
collected by filtration, washed with hexane and dried in air
(yield ∿ 65%).

Method 2. The reddish brown solution resulted from mixing a
solution of 182.4 mg (0.3 mmol) of di-μ-chlorobis[phenylazo-
acetaldoximatopalladium(II)] in 30 ml of benzene and a solution
of 135 mg (0.6 mmol) of phenylazobenzaldoxime in 10 ml of
benzene was heated to boiling (5 minutes) with 2 gms of
anhydrous sodium carbonate (G.R grade). The color of the
solution turned deep green. It was then filtered and the deep
green filtrate was evaporated to small volume and hexane was
added to it when shinning crystals of (phenylazoacetaldoximato)-
(phenylazobenzaldoximato)palladium(II) were deposited. The
crystals were separated by filtration, washed with hexane
and dried in air (yield ∿ 70%).

(ii) (Phenylazoacetaldoximato)(phenylazophenyl-2C,N')palla-
     dium(II):

258.4 mg (0.4 mmol) of trans-μ-dichlorobis(phenyl-
azophenyl-2C,N')dipalladium(II) was dissolved in 50 ml of benzene

and to it was added a solution of 130.5 mg (0.8 mmol) of phenylazoacetaldoxime in 10 ml of benzene. The brown solution thus resulted was heated to boiling with 2 gms of anhydrous sodium carbonate (G.R grade) and stirred (10 minutes). The color of the solution turned deep violet. It was then filtered and the violet filtrate was concentrated to small volume and hexane was added to it. The side of the beaker was scratched when red crystals started separating out. The crystals were filtered, washed with hexane and dried. Recrystallisation from benzene-hexane mixture gave shinning maroon red crystals in ~60% yield.

A Rapid Synthesis of trans-μ-dichlorobis(phenylazophenyl-2C,N')dipalladium(II)

Synthesis of Dichlorobis(azobenzene)palladium(II)[4]:

A solution containing 1.0 gm of Pd(PhCN)$_2$Cl$_2$ in 10 ml of dichloromethane was added to a solution of 2.0 gm of azobenzene in 30 ml of dichloromethane. After standing for 24 hrs, the orange crystals were collected by filtration, washed with cold chloroform and dried in air.

Synthesis of the Cyclopalladated Species:

A mixture of a solution of 270.5 mg (0.5 mmol) of dichlorobis(azobenzene)palladium(II) in 40 ml chloroform and a

solution of 147 mg (0.5 mmol) of sodium tetrachloropalladate(II) in 25 ml of 1:1 aqueous ethanol was heated to reflux for 4 hrs when shinning maroom crystals were collected in the organic layer. After cooling the mixture, the upper (aqueous) layer was removed carefully and the crystals were collected from the organic layer by filtration. They were washed first with water and then with chloroform and finally dried in air. The yield was ∿ 90%.

B. Characterisation of Complexes

This was done by C,H,N microanalysis and metal analysis. Palladium was estimated as dimethylglyoximate after decomposing the complex with aqua regia. Characterisation data for the complexes are set out in Table II.6.

C. Solvents

Benzene was purified by successive shaking with concentrated sulphuric acid (to remove thiophene), sodium bicarbonate solution and water. It was then dried over fused $CaCl_2$ and was finally distilled over sodium. Ethanol was dehydrated by distilling commercial absolute ethanol over quick-lime. Chloroform (ANALAR grade) was used without further purification.

TABLE II.6

CHARACTERISATION DATA OF PALLADIUM(II) COMPLEXES

Compound	MP °C [a]	% C Calc.	% C Found	% H Calc.	% H Found	% N Calc.	% N Found	% Pd Calc.	% Pd Found
Chloro-bridged arylazooximates:									
$Pd_2(Meaao)_2Cl_2$	265	31.66	31.50	2.64	2.71	13.80	13.78	35.03	34.93
$Pd_2(Phaao)_2Cl_2$	>280	42.64	42.81	2.73	2.70	11.48	11.52	29.07	29.10
$Pd_2(p\text{-}tolaao)_2Cl_2$	>280	44.21	44.30	3.18	3.24	11.05	11.10	23.02	28.15
Bromo-bridged arylazooximates:									
$Pd_2(Meaao)_2Br_2$	238-240	27.55	28.10	2.31	2.30	12.05	12.01	30.54	30.53
$Pd_2(Phaao)_2Br_2$	>280	38.01	38.10	2.45	2.51	10.23	10.30	25.92	26.10
$Pd_2(p\text{-}tolaao)_2Br_2$	>280	39.58	39.47	2.85	2.78	9.89	10.05	25.07	25.10

TABLE II.6 (contd.)

Compound	MP°C[a]	% C Calc.	% C Found	% H Calc.	% H Found	% N Calc.	% N Found	% Pd Calc.	% Pd Found
Bis-arylazooximates:									
Pd(Meaao)$_2$	192	44.59	44.20	3.74	3.80	19.51	19.10	24.71	24.80
Pd(Phaao)$_2$	236	56.20	55.90	3.63	3.70	15.14	14.97	19.30	19.18
Pd(p-tolaao)$_2$	247	57.67	58.10	4.15	4.10	14.41	14.28	18.26	18.37
Mixed species:									
Pd(Meaao)(Phaao)	220	51.15	51.90	3.68	3.91	17.05	17.13		
Pd(Meaao)(azbz)	175	53.25	52.89	3.80	3.76	15.53	15.52		

a All melting points reported in this table are uncorrected.

D. Physical Measurements

a. Infrared Spectra

These were recorded either on a Perkin-Elmer 521 or a
Beckman IR-20A recording spectrophotometer. The wavelength
scale was calibrated using a polystyrene film. The far-infrared
spectra were run (mull in nujol) on a modified RIIC FS-620
machine.

b. Electronic Spectra

These were measured on a Cary-14 recording spectrophoto-
meter. Silica cells (matched pairs) of 1 cm pathlength were
used throughout. Spectroscopic quality solvents (benzene and
chloroform) were used for these measurements.

c. Proton Resonance Measurements

Results reported in this and later chapters were
obtained using either a Varian T-60A spectrometer (60 MHZ) or
a Varian EM-390 spectrometer (90 MHZ). Frequencies were measured
by the usual side band technique. $CDCl_3$ and tetramethylsilane
were uniformly used as the solvent and the internal standard
respectively.

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CHAPTER III

BRIDGE-SPLITTING REACTIONS OF

DI-μ-HALOBIS $\left[\text{ARYLAZOOXIMATOPALLADIUM(II)}\right]$

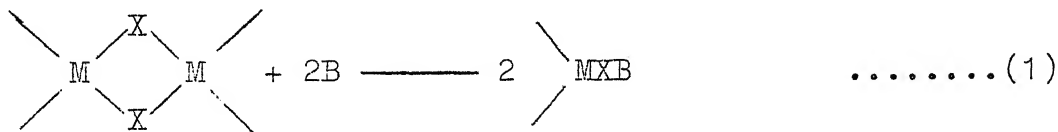WITH LEWIS BASES

CHAPTER III

BRIDGE-SPLITTING REACTIONS OF
DI-μ-HALOBIS [ARYLAZOOXIMATOPALLADIUM(II)]
WITH LEWIS BASES

Abstract: Bridge-splitting reactions of the halo-bridged
arylazooximes $Pd_2(Raao)_2X_2$ with various monodentate and
bidentate Lewis bases have been described. The halo-bridged
complexes $Pd_2(Raao)_2X_2$ undergo facile bridge-splitting
reactions with monodentate amines (am) like ammonia, methylamine,
pyridine, γ-picoline and aniline to yield [(Raao)Pd(am)X]
complexes. When heated around $200^{O}C$, the [(Raao)Pd(am)X]
complexes (where R = aryl; am = pyridine, γ-picoline and
aniline) lose 'am' to regenerate the halo-bridged species.
Since the bridge-cleavage reaction is fast with bulky donors
like 2,6-lutidine and triphenylarsine, the entering donor
molecule in [(Raao)Pd(am)X] is expected to occupy the position
trans- to the azo-end of the arylazooximato (aao) chelate ring.
Triphenylarsine splits the halogen-bridge in $Pd_2(Raao)_2X_2$
to produce [(Raao)Pd(AsPh_3)X]. In no case excess amine (or
triphenylarsine) can open the aao chelate ring. With bidentate

amines like o-phenanthroline and ethylenediamine, $Pd_2(Raao)_2X_2$ yields ionic species of the type $\left[(Raao)Pd(N-N)\right]^+ X^-$. Reaction of $Pd_2(Raao)_2Cl_2$ with $Ph_4As^+Cl^-$ also leads to the formation of ionic species namely $Ph_4As^+\left[(Raao)PdCl_2\right]^-$. All these complexes behave as 1:1 electrolytes in solution. The bridge-split products exhibit an intense band at ~ 500 nm ($\epsilon \sim 5000$) which is characteristic of the moiety $(Raao)Pd\diagdown$. In $\left[(Raao)Pd(donor)X\right]$ complexes ν_{N-O} and ν_{Pd-Cl} appear in the range 1250-1300 cm^{-1} and at ~ 350 cm^{-1} respectively. $Ph_4As^+\left[(Raao)PdCl_2\right]^-$ exhibits ν_{Pd-Cl}(cis) at 330 and 300 cm^{-1}. The methyl group of the chelated aao fragment resonates at $\delta \sim 2.3$ ppm in $\left[(Raao)Pd(donor)X\right]$ complexes. Stoichiometric amount of triarylphosphines (PAr_3) cleave the halogen-bridge in $Pd_2(Raao)_2X_2$ to yield complexes of the type $\left[(Raao)Pd(PAr_3)X\right]$. Further addition of phosphines opens the aao chelate ring at the azo-end and in solution an equilibrium exists between the open-ring and closed-ring species. Triarylphosphines displace coordinated am's from $\left[(Raao)Pd(am)X\right]$ to produce $\left[(Raao)Pd(PAr_3)X\right]$ The $\left[(Raao)Pd(PAr_3)X\right]$ complexes can also be synthesised by mixing $Pd(Raao)_2$ and trans-$\left[(PAr_3)_2PdX_2\right]$ (molar ratio 1:1) in benzene or chloroform.
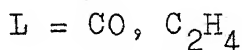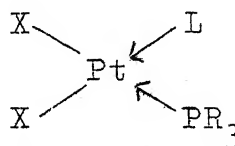
III.1 <u>INTRODUCTION</u>

A major reaction of halo-bridged palladium(II) (and platinum(II)) species is the facile cleavage of the bridge by Lewis bases:

$$\diagdown \!\!M\!\!\diagup^{X}_{X}\!\!M\!\!\diagup \quad + \; 2B \;\longrightarrow\; 2 \;\rangle MXB \qquad \ldots\ldots(1)$$

Mann and Purdie demonstrated this reaction as early as 1936 with halo-bridged complexes of phosphines and arsines. The Lewis bases were different monodentate and bidentate amines. Since then bridge-splitting reactions have been observed to be of quite general occurrence. Selected examples[1-11] are presented in Table III.1. Usually the ease of bridge-splitting follows the order Cl $\sim$ Br $\rangle$ I. In the case of iodo-bridge it is often difficult to isolate the bridge split products. When the original ligand(s) on the metal is (are) monodentate, the product isolated after bridge-splitting is usually <u>trans</u> (structure I) except in caseswhere two strong <u>trans</u>-labilising groups are present e.g. II.

L = CO, C_2H_4

I   II

SUMMARY OF BRIDGE-SPLITTING REACTIONS

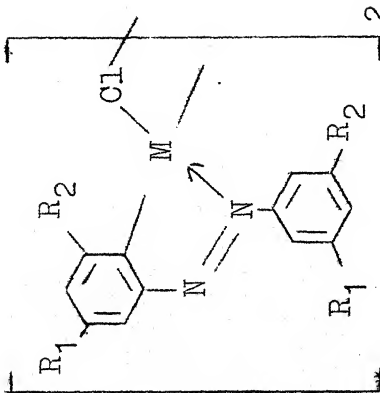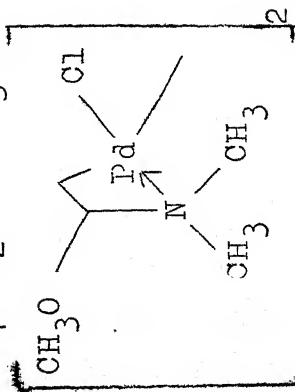| System	Base	Comments	Ref.
$[(R_3E)_2Pd_2Cl_4]$ $E = P, As$	$NH_3, PhNH_2,$ ethylenediamine(en) 2,2'-dipyridyl(dipy)	Products are $[(R_3E)Pd(am)Cl_2]$ (am = $NH_3, PhNH_2$), $[(R_3E)Pd(en)Cl]^+Cl^-$ and $[(R_3E)_2PdCl_2]+[(dipy)PdCl_2]$. In $[(R_3E)Pd(NH_3)Cl_2]$, NH_3 is weakly held. $[L(am)PdCl_2]$ complexes can be isolated only when the donor atom in L is P or As. When L = R_2S, R_2Se or R_2Te, disproportionation of the bridge-split products leads to $[L_2PdX_2]$ and $[(am)_2PdX_2]$. With L = C_2H_4, disproportionation occurs even at $-70°C$.	1,2,3
$[L_2Pt_2X_4]$ L = C_2H_4, amines, $PR_3, AsR_3, SbR_3,$ R_2S, R_2Se, R_2Te	p-toluidine and other amines, CO, C_2H_4	The bridge-split products are claimed to have trans- configuration. The reversible reaction $[L_2Pt_2X_4] + 2$ am $\rightleftharpoons$ $2[LPt(am)X_2]$ is shifted to left for weak or sterically hundered amines. Bridge-split products are either trans-(L≠amine) or cis-trans-mixture (L = amine). With bases like CO or C_2H_4, cis- products are obtained. When L = R_2S, R_2Se or R_2Te, disproportionation of the bridge-split products gives $[L_2PtX_2]$ and $[(am)_2PtX_2]$.	4,5,6,'

Table III.1 contd....

System	Base	Comments	Ref.
M = Pd, Pt R$_1$= R$_2$= H, CH$_3$	amines	Products are where L = amines	8
	aniline, PFh$_3$	Same as above	9

Table III.1 contd..

System	Base	Comments	Ref.
$\left[Pd(C-N)X\right]_2$ C–N = azobenzene-2-C,N; NN–dimethylbenzyl–amine-2-C,N. X = Cl, Br	mono– and bidentate ligands containing donor atoms of gr VB.	Products are (N→Pd with C and X–L) and N–C–Pd–X (with L above and below; with L = PR₃ only). With bidentate ligands (en, diphos etc) the bridge-splitting reaction produces ionic complexes e.g. $\left[\text{(N→Pd←C) (L→Pd←L)}\right]^{+}$ X⁻.	10
$\left[Pd(C-N)X\right]_2$ C–N = acetophenone–hydrazone. X = Cl, Br, I	pyridine, PR₃, AsR₃, SbR₃, en and diphos. diphos = 1,2–bis(diphenyl–phosphino)ethane.	Same as above except that with diphos the product is (C→Pd←P P→Pd←C with X, X, N, N).	11
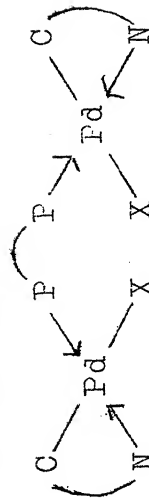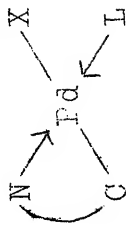
When the original ligand in the halo-bridged complex
is bidentate and symmetrical (a case not well-documented) there
is no structural ambiguity in the bridge-split product. However
in the case of unsymmetric bidentate ligands, two isomers, III
and IV, are possible. This problem will be considered in further
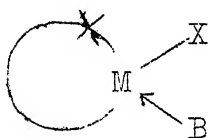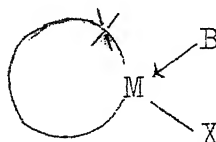
III   IV

detail later since it is of direct import in relation to the
work described in this chapter. This work pertains to the
study of bridge-splitting reactions of the halo-bridged
arylazooximates of palladium(II) by amines, phosphines and
arsines. We wish to note that to our knowledge these are the
first examples of bridge-splitting reactions in which the
unsymmetric bidentate ligand binds through two nitrogen atoms
in the mother compound. In the cyclopalladated species whose
bridge-splitting reactions are reported, the bonding is through
a carbon atom and a nitrogen atom.

III.2 RESULTS AND DISCUSSION

## A. Reactions With Monodentate Amines

a. The General Reaction

The following amines were used: ammonia, methylamine,
pyridine (abbreviated hereafter as py), γ-picoline (abbreviated

hereafter as, γ-pic), aniline and imidazole. In benzene or dichloromethane, stoichiometric amounts of these amines cleave the halogen-bridge readily to produce complexes of the type $[(Raao)Pd(am)X]$:

$$Pd_2(Raao)_2X_2 + 2\ am \longrightarrow 2[(Raao)Pd(am)X] \qquad \ldots\ldots\ldots(2)$$
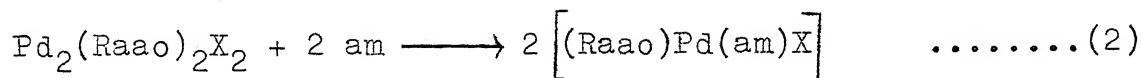
X = Cl, Br   am = amine

A number of $[(Raao)Pd(am)X]$ complexes have been isolated as violet crystalline solids which are quite soluble in benzene, chloroform and dichloromethane and sparingly soluble in methyl and ethyl alcohol. When heated around $200^{\circ}C$ (the range is $210-225^{\circ}C$) the $[(Raao)Pd(am)X]$ complexes where R = Ph or p-tol, X = Cl or Br and am = py, γ-pic, 2,6-lutidine or aniline, loose the amine molecule (with a characteristic color-change from violet to purple) and the halo-bridged complexes are regenerated i.e.

$$2[(Raao)Pd(am)X] \xrightarrow{\sim200^{\circ}C} Pd_2(Raao)_2X_2 + 2\ am \qquad \ldots\ldots(3)$$
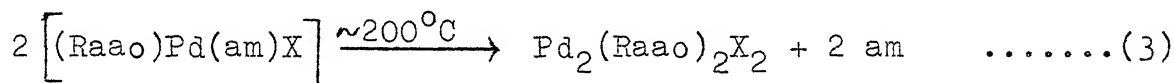
Complexes of the type $[(Meaao)Pd(am)X]$ however, melt without the loss of amine. A few reports[1,2,7] are known where such dimerisation occurs with the loss of coordinating ligands.

It has already been pointed out in Chapter II that the moiety V can be distinguished by its electronic spectrum where


V
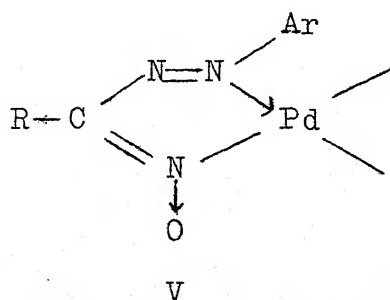
an intense band around 500 nm with an extinction coefficient of
~5000 per Pd atom is always observed. The halo-bridged arylazo-
oximates have in general an intense band at ~540 nm with an
extinction coefficient of ~5000 per Pd atom. The bridged-
cleavage is characterised by a blue shift of ~30 nm (color changes
from violet or purple to deep red) of the band with little
change in extinction coefficient when the amines are added to
the solution of the halo-bridged arylazooximates in benzene or
dichloromethane. The $\left[(Raao)Pd(am)X \right]$ complexes crystallise out
on concentrating these solutions. All these amines fail to
react further to open the arylazooximato chelate ring even when
used in excess. This has been checked by monitoring the elect-
ronic spectra of the bridge-split products with different ratios
of the amines in benzene solution when no further change in the
electronic spectra is observed. Similar behavior of amines has
been reported in the bridge-splitting reactions of the halo-
bridged cyclopalladated complexes[10,11].

b. Reaction with Sterically Hindered Amine

For the bridge-split products, two structures are
possible namely VI and VII.
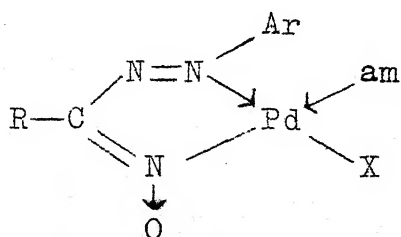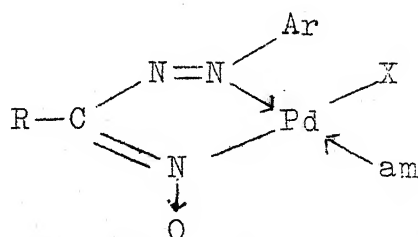
VI   VII

In all these bridge-splitting reactions, however, chromatography of the bridge-split product on alumina failed to detect the presence of more than one separable species. The room temperature pmr spectra of $\left[(\text{Raao})\text{Pd(am)X}\right]$ complexes show sharp and single resonance signal for each group. In structure VI, quite a bit of steric crowding will be there if a bulky amine is used. On bulky amine namely 2,6-lutidine was to check this point. 2,6-lutidine cleaves the bridge extremely fast. This observation suggests that the entering amine most possibly occupies the position <u>trans-</u> to the azo-end of the arylazooximato chelate ring i.e. structure VII. If structure VI is to be accepted, the complex $\left[(\text{Raao})\text{Pd}(2,6\text{-lutidine})\text{X}\right]$ should be in specific 'locked' configuration (with the two aromatic rings and two methyl groups properly oriented) which is quite unlikely. Further evidence in favour of structure VII for the bridge-split products is available from the reactions of the halo-bridged arylazooximates with phosphines which will be discussed later.

c. Electronic Spectra of the $\left[(\text{Raao})\text{Pd(am)x}\right]$ Complexes

All the $\left[(\text{Raao})\text{Pd(am)X}\right]$ complexes have uniformly one intense band (characteristic of the moiety V) around 500 nm. The positions and intensities of this band for complexes with different R, am and X are listed in Table III.2 and two representative spectra are shown in Fig. III.1. Some general

TABLE III.2

POSITIONS (λ nm) AND INTENSITIES (ϵ M^{-1}cm^{-1}) OF THE NEAR 500nm BAND OF $\left[(Raao)Pd(am)X\right]$ COMPLEXES IN BENZENE AT ROOM TEMPERATURE

COMPOUND	$\lambda(\epsilon)$
$\left[(Meaao)Pd(NH_3)Cl\right]$	512 (5750)
$\left[(Meaao)Pd(NH_2CH_3)Cl\right]$	505 (6100)
$\left[(Meaao)Pd(NH_2C_6H_5)Cl\right]$	515 (5500)
$\left[(Meaao)Pd(py)Cl\right]$	520 (5350)
$\left[(Meaao)Pd(\gamma\text{-pic})Cl\right]$	520 (6200)
$\left[(Meaao)Pd(imidazole)Cl\right]$	515 (4500)
$\left[(Meaao)Pd(NH_2C_6H_5)Br\right]$	515 (5800)
$\left[(Meaao)Pd(py)Br\right]$	520 (5400)
$\left[(Meaao)Pd(\gamma\text{-pic})Br\right]$	520 (5800)
$\left[(Phaao)Pd(py)Cl\right]$	540 (5500)
$\left[(Phaao)Pd(\gamma\text{-pic})Cl\right]$	540 (5300)
$\left[(p\text{-tolaao})Pd(py)Cl\right]$	555 (5350)
$\left[(p\text{-tolaao})Pd(\gamma\text{-pic})Cl\right]$	555 (5450)
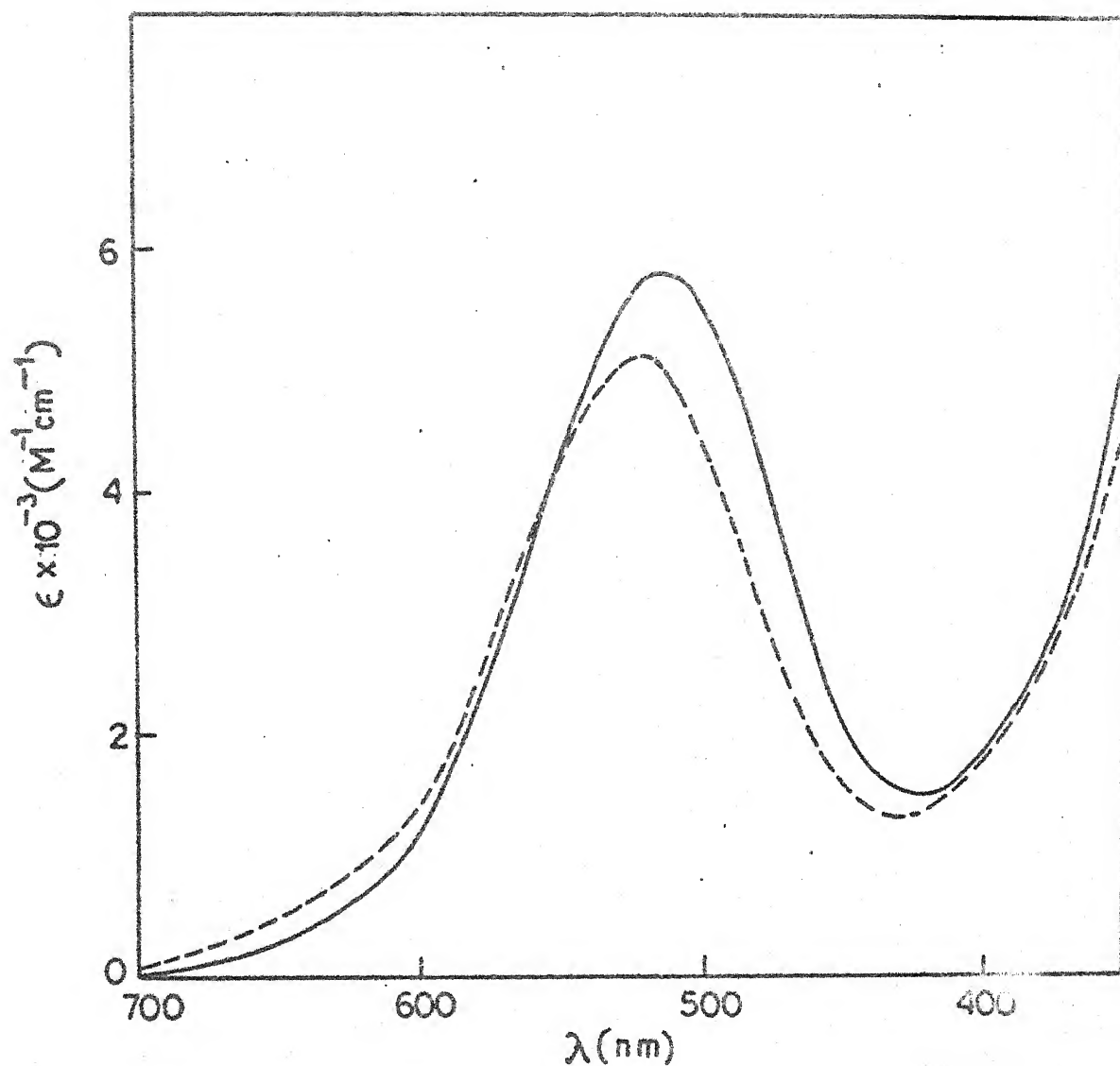
FIG III.1. ELECTRONIC SPECTRA OF $[(Meaao)Pd(NH_3)Cl]$ (———)
AND $[(Meaao)Pd(py)Cl]$ (- - - -) IN BENZENE.

observations emerge from a close scrutiny of the peak positions
of the band which are as follows:

(1) The position of the band maximum λ_{max} varies
slightly with am. For example, with am = NH_3 and py, the peak
positions are at 512 nm and 520 nm respectively.

(2) λ_{max} is rather insensitive to X.

(3) As R changes from alkyl to aryl, a red shift in
λ_{max} is observed.

d. Infrared Spectra

The infrared spectra of the (Raao)Pd(am)X complexes
exhibit characteristic patterns in the range 1600-1000 cm^{-1}
(Fig. III.2 and Fig. III.3). ν_{N-O} appears in the range
1250-1300 cm^{-1} and is usually very strong. ν_{Pd-Cl} absorptions
have been located around 350 cm^{-1} (Table III.3). As expected
this frequency is absent in the corresponding bromo-compounds.
Specific aspects of the infrared spectra of a few selected
complexes are discussed below in greater detail .

(i) $\left[(Meaao)Pd(am)Cl \right]$ where am = NH_3, CH_3NH_2 or $C_6H_5NH_2$.

Only the N-H vibrations will be discussed.
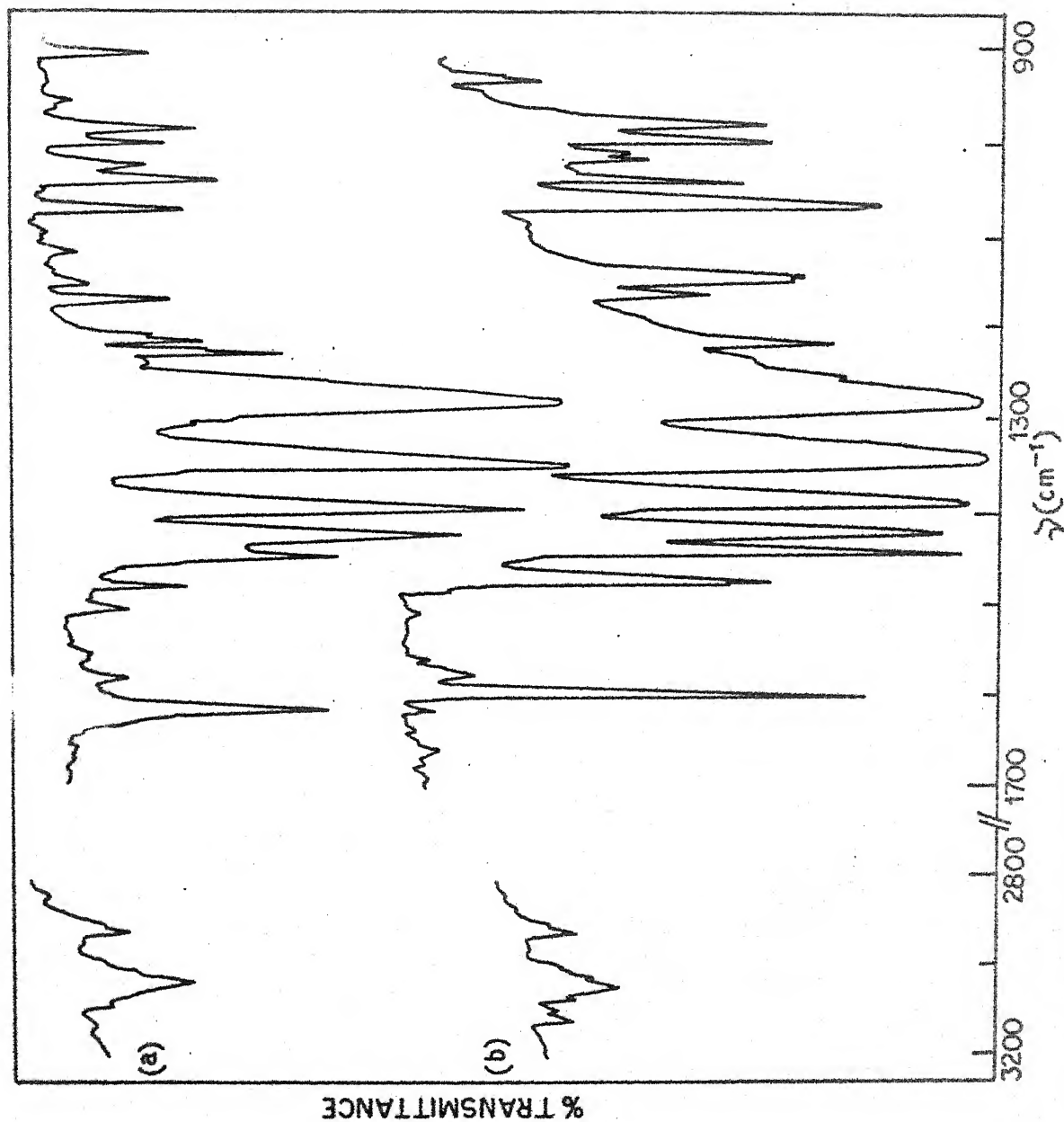
FIG. III . 2 . PARTIAL INFRARED SPECTRA OF (a) [(Meaao)Pd(α-pic)Cl] AND (b) [(Meaao)Pd(py)Br] IN KBr (DISC).
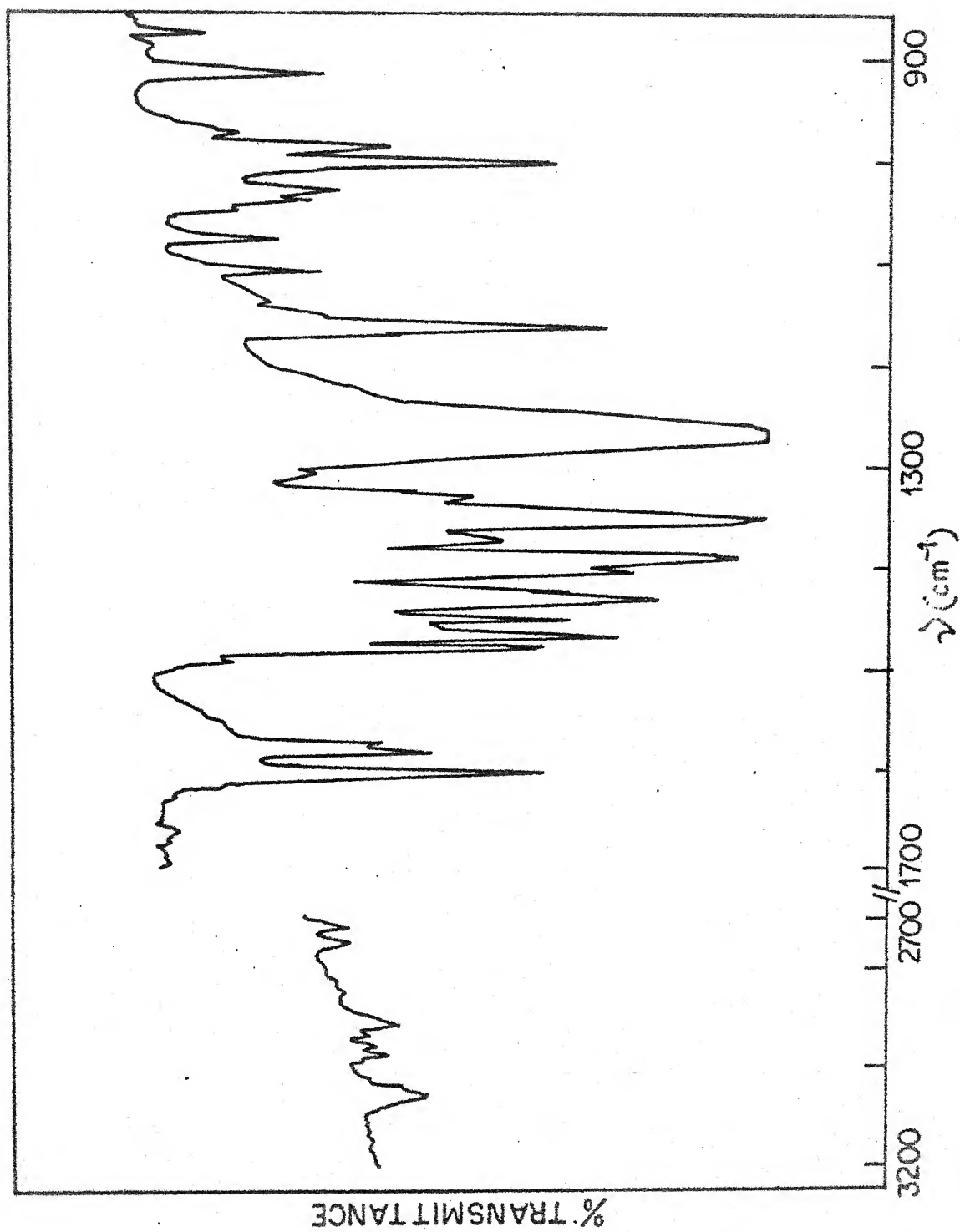
FIG III. 3. PARTIAL INFRARED SPECTRUM OF $\left[(Meaao)Pd(2,6-lut)Cl \right]$ IN KBr(DISC).

TABLE

INFRARED DATA OF $\left[(\text{Raao})\text{Pd}(\text{am})\text{X}\right]$ COMPLEXES IN KBr DISCS (FREQUENCIES ARE IN cm^{-1})

Compound	$\nu_{\text{C-H}}$	$\nu_{\text{N-O}}$	$\nu_{\text{Pd-Cl}}$	Other assigned vibrations
$\left[(\text{Meaao})\text{Pd}(\text{NH}_3)\text{Cl}\right]$	3050(m), 2920(w)	1260(vs)	352(m)	$\nu_{\text{N-H}}$ 3280 (s,br) 3220; δ_{NH_2}(as) 1620(br); δ_{NH_2}(s) 1225(s)
$\left[(\text{Meaao})\text{Pd}(\text{NH}_2\text{CH}_3)\text{Cl}\right]$	3080(m), 2930(m)	1275(vs)	355(s)	$\nu_{\text{N-H}}$ 3260(s) 3200(m); δ_{NH_2}(as) 1585(s); $\nu_{\text{C-N}}$ 1075(s)
$\left[(\text{Meaao})\text{Pd}(\text{NH}_2\text{C}_6\text{H}_5)\text{Cl}\right]$	3070(m), 2920(w)	1270(vs)	355(s)	$\nu_{\text{N-H}}$ 3260(s) 3200(m); δ_{NH_2} 1565(m)
$\left[(\text{Meaao})\text{Pd}(\text{py})\text{Cl}\right]$	3050(m), 2920(w)	1275(vs)	350(m)	
$\left[(\text{Meaao})\text{Pd}(\gamma\text{-pic})\text{Cl}\right]$	3040(m), 2920(w)	1275(vs)	350(s)	
$\left[(\text{Meaao})\text{Pd}(\text{imidazole})\text{Cl}\right]$	3050(m), 2930(w)	1275(vs)	360(m)	$\nu_{\text{N-H}}$ 3270(s) 3120(m)
$\left[(\text{Meaao})\text{Pd}(2,6\text{-lutidine})\text{Cl}\right]$	3060(m), 2960(w) 2910(w).	1270(vs)	340(m)	
$\left[(\text{Meaao})\text{Pd}(\text{NH}_2\text{C}_6\text{H}_5)\text{Br}\right]$	3060(m), 2920(w)	1275(vs)	a	$\nu_{\text{N-H}}$ 3270(s) 3200(m); δ_{NH_2} 1560(s)

Compound	ν C-H	ν N-O	ν Pd-Cl	Other assigned vibrations
[(Meaao)Pd(py)Br]	3060(m), 2920(w)	1270(vs)	a	
[(Meaao)Pd(γ-pic)Br]	3050(m), 2920(m)	1275(vs)	a	
[(Phaao)Pd(py)Cl]	3050(m)	1235(s)	b	
[(Phaao)Pd(γ-pic)Cl]	3060(m), 2920(w)	1240(s)	b	
[(Phaao)Pd(2,6-lutidine)Cl]	3050(m), 2960(w), 2020(w)	1235(vs)	340(m)	
[(p-tolaao)Pd($NH_2C_6H_5$)Cl]	3060(m), 2920(w)	1235(s)	355(m)	ν N-H 3240(s), 3180(m); δ_{NH_2} 1565(s)
[(p-tolaao)Pd(py)Cl]	3060(m), 2910(w)	1240(s)	350(w)	
[(p-tolaao)Pd(γ-pic)Cl]	3050(m), 2920(w)	1245(s)	355(w)	
[(p-tolaao)Pd(2,6-lutidine)Cl]	3050(m), 3030(w), 2970(w), 2910(m)	1235(s)	335(m)	
[(p-tolaao)Pd(γ-pic)Br]	3060(m), 2910(w)	1245(s)	a	
[(p-tolaao)Pd(2,6-lutidine)Br]	3050(w), 2910(w)	1230(s)	a	

a = weak; m = medium; s = strong; vs = very strong and br = broad.

a absent.

b not assigned.

Characteristic N-H frequencies (in cm^{-1}) are set out below.

		$\nu_{N-H(as)}$	$\nu_{N-H(s)}$	$\delta_{NH_2(as)}$
$[(Meaao)Pd(NH_3)Cl]$	Solid (KBr disc)	3330 (broad)	3255 (broad)	1620 (broad)
	Solution (in $CHCl_3$)	3360	3290	1600
$[(Meaao)Pd(NH_2CH_3)Cl]$	Solid (KBr disc)	3260	3200	1585
$[(Meaao)Pd(NH_2C_6H_5)Cl]$	Solid (KBr disc)	3260	3200	1565

The complex $[(Meaao)Pd(NH_3)Cl]$ exhibits broad ν_{N-H} absorptions which shift to the higher energy side in chloroform solution. Also, in solution, δ_{NH_2} moves to the lower energy region. Thus it seems that the complex is associated in the solid state by intermolecular hydrogen bonding through N-H bonds. Similar association has been reported for $[L(am)PtCl_2]$ complexes[6]. The broad antisymmetric deformation vibration around 1600 cm^{-1} in Pd(II) complexes has been pointed out by Layton et al[12]. This could arise either from steric hindrance to free rotation of the $-NH_3$ group about the M-N bond[13] or from ligand-ligand interaction through filled d-orbital on the metal[14]. The ν_{N-H} absorptions of the complex $[(Meaao)Pd(NH_2CH_3)Cl]$ are quite sharp

even in the solid state and are not shifted appreciably in
chloroform solution. The compound does not seem to be much
associated in the solid state. Similar is the case with
$\left[(\text{Meaao})\text{Pd}(\text{NH}_2\text{C}_6\text{H}_5)\text{Cl}\right]$. The N-H stretching frequencies, in
all the three cases, follow very closely the relationship(3)
suggested by Bellamy and Williams[15] for free or coordinated
NH_2 group where both H's are equivalent

$$\nu_{(s)} = 345.53 + 0.876\,\nu_{(as)} \qquad\qquad \text{........(3)}$$

(ii) $\left[(\text{Raao})\text{Pd}(\text{am})\text{X}\right]$ where R = Me, Ph or P-tol; am = pyridine
or γ-picoline; X = Cl or Br.

Characteristic strong bands at 1600, 1440 and 1215 cm^{-1}
and medium bands around 1050-1000 cm^{-1} confirm the presence of
coordinated pyridine molecule[16] in the $\left[(\text{Raao})\text{Pd}(\text{py})\text{X}\right]$ complexes.
Coordinated γ-picoline[17] was identified by strong absorptions
at $\sim$1620, $\sim$1240 and $\sim$810 cm^{-1} in the infrared spectra of the
$\left[(\text{Raao})\text{Pd}(\gamma\text{-pic})\text{X}\right]$ complexes. In the case of $\left[(\text{p-tolaao})\text{Pd}\right.$
$\left.(\gamma\text{-pic})\text{X}\right]$ X = Cl, Br, where there are two parasubstituted
phenyl groups (one in arylazooxime ligand and one in γ-picoline),
two strong absorptions at 815 cm^{-1} (for Raao ligand) and
805 cm^{-1} (for γ-picoline) are observed.

(iii) $\left[(\text{Meaao})\text{Pd}(\text{imidazole})\text{Cl}\right]$

Imidazole is known to bind to different metal ions
through its tertiary nitrogen **atom** and in such complexes broad
and strong $\nu_{\text{N-H}}$ absorption[18] appears in the range 3100-3400 cm^{-1}.

Recently the binding of guanosine[19] and adenosine[20] to palladium has been shown to be through the tertiary nitrogen atom (N_7) of the purine base. In the chelate $\left[(Meaao)Pd(imidazole)Cl\right]$, palladium is also bound to the tertiary nitrogen atom of the imidazole ligand and the complex exhibits a strong and somewhat broad ν_{N-H} absorption with band maximum at 3270 cm^{-1}.

e. Proton Magnetic Resonance Spectra

The ^{1}H chemical shifts of the $\left[(Raao)Pd(am)X\right]$ complexes are set out in Table III.4 and a few representative spectra are shown in Fig. III.4 and III.5. All the spectra exhibit expected resonance patterns and are consistent with the compositions proposed. The methyl group of phenylazoacetaldoximato fragment uniformly gives a sharp signal at $\delta \sim 2.3$ ppm. This signal varies slightly with changes in am or X. The NH_2 signal of coordinated aniline in $\left[(Meaao)Pd(NH_2C_6H_5)X\right]$ complexes, as expected, appears at low field $\delta \sim 5.2$ ppm (for free aniline $\delta_{NH_2} = 3.66$ ppm). The methyl groups of coordinated 2,6-lutidine resonate at appreciably lower field $\delta = 3.13$ ppm (δ CH_3 of free 2,6-lutidine = 2.52 ppm) whereas the methyl signal of γ-picoline is shifted slightly to lower field (from $\delta = 2.3$ ppm to $\delta = 2.4$ ppm) on coordination. Most possibly the larger shift of the methyl signal in the case of 2,6-lutidine is due to the closer proximity of the methyl groups to the donor center. The methyl signal of phenylazo-p-tolualdoximato fragment has been found to be quite insensitive towards changes in am or X (Table III.4).
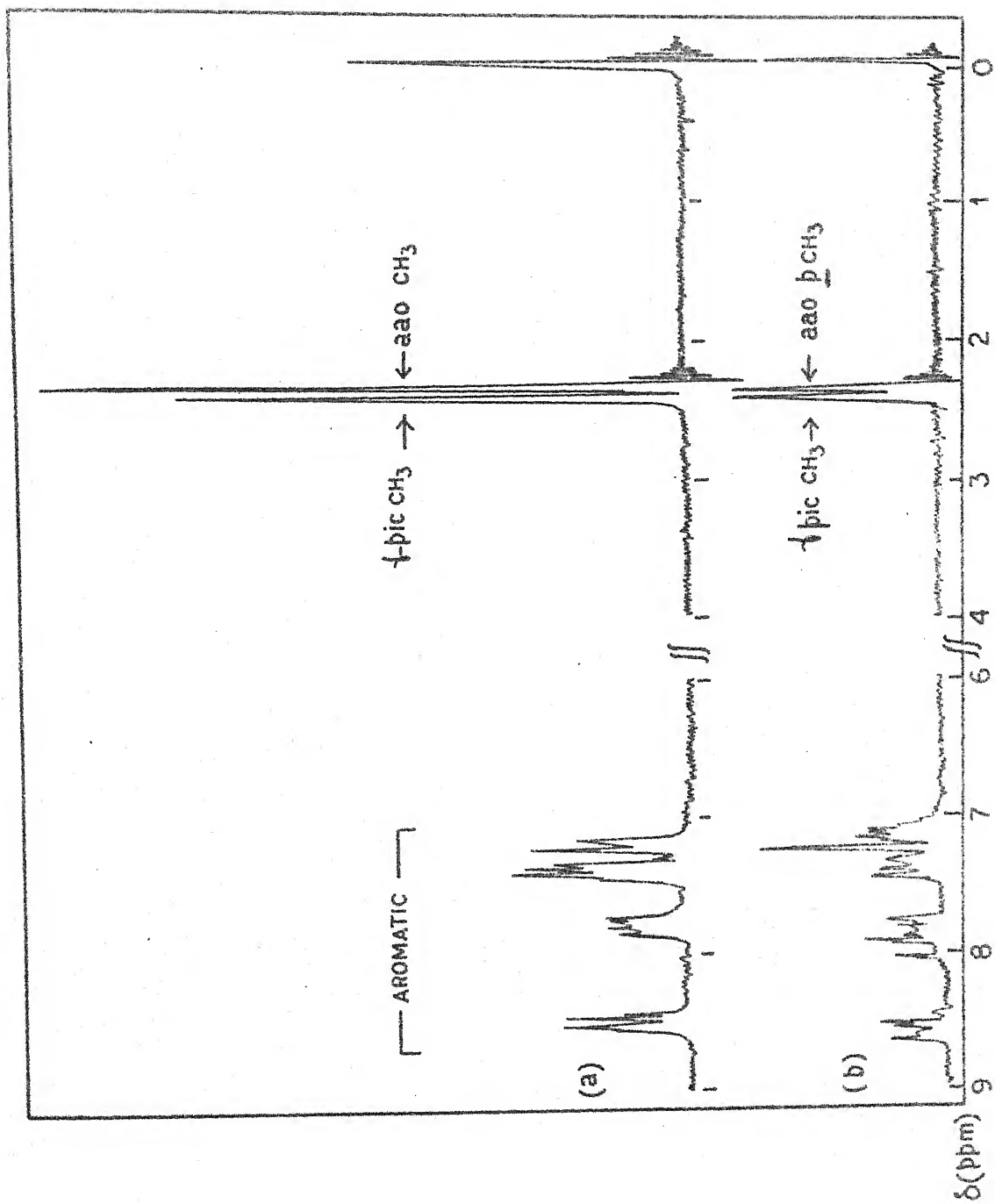
FIG III. 4. PMR SPECTRA OF (a) [(Me₄ao)Pd (4-pic)cl] AND (b) [(p-tolaao)Pd (4-pic)Cl] IN CDCl₃.
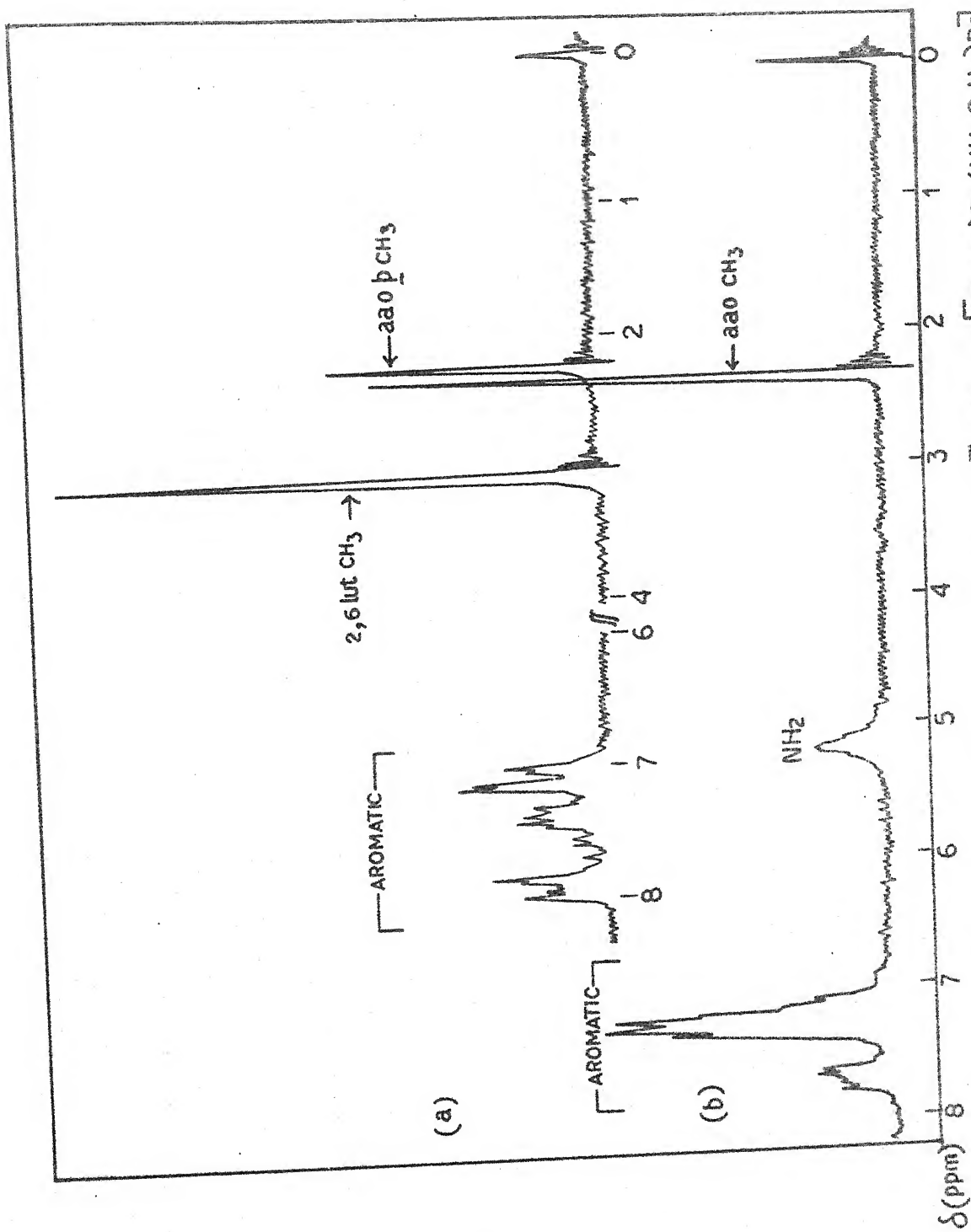
FIG. III.5 PMR SPECTRA OF (a) $[(p\text{-tolaao})Pd(2,6\text{-lut})Cl]$ AND (b) $[(Meaao)Pd(NH_2C_6H_5)Br]$ IN $CDCl_3$.

TABLE III.4

[1]H CHEMICAL SHIFTS[a] OF $\left[(Raao)Pd(am)X\right]$ COMPLEXES

SOLVENT: $CDCl_3$

Compound	Group	Chemical Shift δ (ppm)
$\left[(Meaao)Pd(NH_2C_6H_5)Cl\right]$	aao CH_3	2.33[b]
	NH_2	5.27
$\left[(Meaao)Pd(NH_2C_6H_5)Br\right]$	aao CH_3	2.36
	NH_2	5.20
$\left[(Meaao)Pd(py)Cl\right]$	aao CH_3	2.33
$\left[(Meaao)Pd(py)Br\right]$	aao CH_3	2.36
$\left[(Meaao)Pd(\gamma-pic)Cl\right]$	aao CH_3	2.30
	γ-pic CH_3	2.37
$\left[(Meaao)Pd(\gamma-pic)Br\right]$	aao CH_3	2.33
	γ-pic CH_3	2.42
$\left[(Meaao)Pd(NH_2CH_3)Cl\right]$	aao CH_3	2.33
	amine CH_3	2.60[c]
$\left[(Meaao)Pd(2,6-lut)Cl\right]$	aao CH_3	2.29
	2,6-lut CH_3	3.13
$\left[(Phaao)Pd(\gamma-pic)Cl\right]$	γ-pic CH_3	2.43
$\left[(p-tolaao)Pd(py)Cl\right]$	p-CH_3 (aao)	2.37
$\left[(p-tolaao)Pd(py)Br\right]$	p-CH_3 (aao)	2.37

TABLE III.4 (contd.)

Compound	Group	Chemical Shift δ (ppm)
[(p-tolaao)Pd(γ-pic)Cl]	p-CH$_3$(aao)	2.37
	γ-pic CH$_3$	2.43
[(p-tolaao)Pd(γ-pic)Br]	p-CH$_3$(aao)	2.37
	γ-pic CH$_3$	2.43
[(p-tolaao)Pd(2,6-lut)Cl]	p-CH$_3$(aao)	2.33
	2,6-lut CH$_3$	3.17
[(p-tolaao)Pd(2,6-lut)Br]	p-CH$_3$(aao)	2.33
	2,6-lut CH$_3$	3.17

[a] Aromatic protons give signals in the region 6.70-8.50 ppm and are not tabulated.

[b] Chemical shift of CH$_3$ group in HMeaao is 2.37 ppm.

[c] Center of a triplet.

B. Reactions With Bidentate Amines

a. The General Reaction

Two bidentate amines were used namely o-phenanthroline (abbreviated hereafter as phen) and ethylenediamine (abbreviated hereafter as en). Stoichiometric amount of en in dichloromethane or phen in methanol cleaves the halogen-bridge readily to produce complex of the type VIII e.g.

$$Pd_2(Raao)_2Cl_2 + 2\ L\!-\!L \longrightarrow 2\ \left[R\!-\!C \begin{array}{c} N = N \\ \\ N \end{array} \!\!\!\!\!\!\!\!\!\!\!\! \overset{Ar}{\underset{O}{\Big\downarrow}} Pd \begin{array}{c} L \\ \\ L' \end{array} \right]^{+} Cl^{-} \quad ..(4)$$

VIII
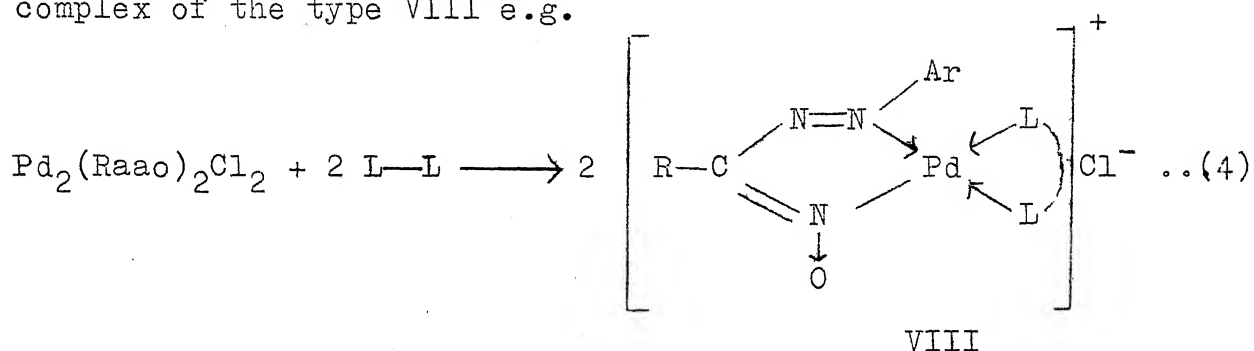
Similar bridge-splitting reactions with bidentate amines are reported in case of a few halo-bridged orthopalladated complexes[10,11]. The reaction (4) was studied in detail with R = Me only because the halo-bridged complexes with R = Ar are sparingly soluble in organic solvents. Excess amine in both the cases leads to complicated reactions yielding gummy products. In the o-phenanthroline reaction which is performed in methanol (vide experimental section), the compound that crystallises out has the composition $\left[(Meaao)Pd(phen)\right]Cl, CH_3OH$. Both the complexes, $\left[(Meaao)Pd(phen)\right]Cl, CH_3OH$ and $\left[(Meaao)Pd(en)\right]Cl$ are violet crystalline solids which are soluble in methanol, ethanol, acetone, acetonitrile and sparingly soluble in water. The molar

electrical conductivities of the complexes in methanol lie in the range 80-100 $ohm^{-1}cm^2mol^{-1}$ (Table III.5). The range prescribed[21] for 1:1 electrolytes in methanol is 80-115 $ohm^{-1}cm^2mol^{-1}$. Clearly the complexes under discussion are 1:1 electrolytes. When the complexes VIII (R = Me) are treated with excess $NaClO_4$ in methanol, the corresponding perchlorates are precipitated as violet crystalline solids. The perchlorate salts are soluble in acetonitrile and acetone and sparingly soluble in alcohols. The molar electrical conductivities of the perchlorates in acetonitrile confirm them as 1:1 electrolytes (Table III.5).

b. Spectral Data of the Complexes

In the electronic spectra of the complexes VIII (R = Me) in methanol, the expected intense band around 500 nm with $\epsilon \sim 5000$ (characteristic of the moiety V) is observed (Table III.6). The infrared data of the complexes $[(Meaao)Pd(L-L)]X$ where L-L = phen or en, X = Cl^- or ClO_4^- are set out in Table III.7 and two representative spectra are shown in Fig. III.6. The infrared spectra of $[(Meaao)Pd(phen)]X$, X = Cl^- and ClO_4^-, exhibit strong bands at 1620, 1575, 1425 and 860 cm^{-1} which are characteristics of coordinated o-phenanthroline[22]. In the infrared spectra of $[(Meaao)Pd(en)]X$, X = Cl^- and ClO_4^-, three strong absorptions are observed in the ν_{N-H} region (Table III.7). Similar observation has been reported for $[Pd(en)_2]Cl_2$ also[23]. The pmr spectra could not be recorded because of insolubility of the complexes VIII (R = Me) in $CDCl_3$.

TABLE III.5

MOLAR ELECTRICAL CONDUCTIVITIES (Λohm^{-1}cm^{2}mol^{-1}) OF $\left[(\text{Meaao})\text{Pd(L-L)}\right]$Cl COMPLEXES IN METHANOL AND $\left[(\text{Meaao})\text{Pd(L-L)}\right]ClO_4$ COMPLEXES IN ACETONITRILE AT 25°C.

Compound	Concentration(M) x 10^3	Λ
$\left[(\text{Meaao})\text{Pd(phen)}\right]Cl, CH_3$OH	0.98	88
$\left[(\text{Meaao})\text{Pd(en)}\right]$Cl	1	98
$\left[(\text{Meaao})\text{Pd(phen)}\right]ClO_4$	1.01	127
$\left[(\text{Meaao})\text{Pd(en)}\right]ClO_4$	1.02	123

TABLE III.6

ELECTRONIC SPECTRAL DATA OF $\left[(\text{Meaao})\text{Pd(L-L)}\right]$Cl COMPLEXES IN METHANOL AT ROOM TEMPERATURE (λ = BAND MAXIMUM IN nm; ϵ = EXTINCTION COEFFICIENT IN M^{-1}cm^{-1}).

Compound	λ (ϵ)
$\left[(\text{Meaao})\text{Pd(phen)}\right]Cl, CH_3$OH	505 (4000)
$\left[(\text{Meaao})\text{Pd(en)}\right]$Cl	500 (6300)

% TRANSMITTANCE

γ (cm^{-1})
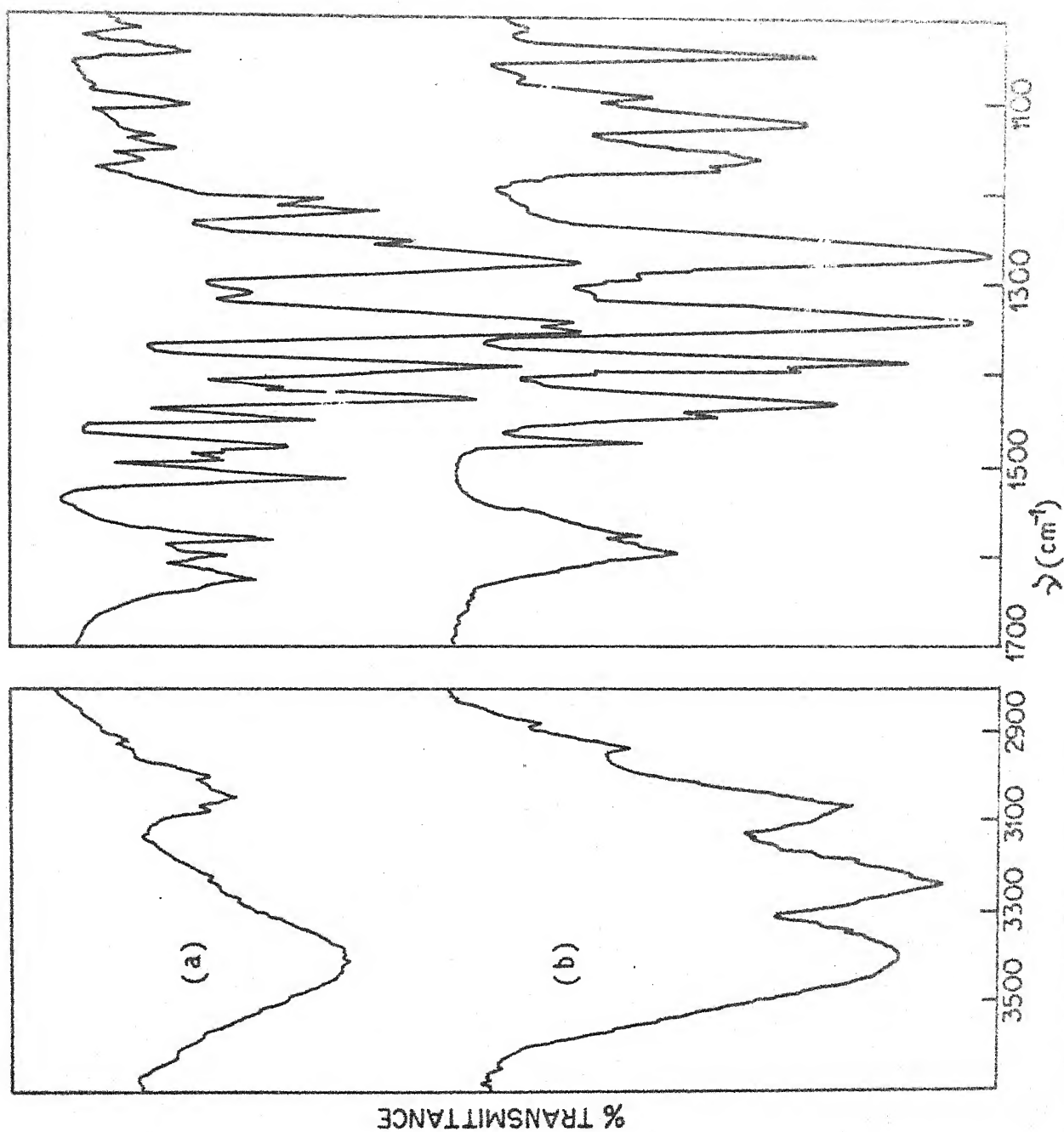
FIG III.6 PARTIAL INFRARED SPECTRA OF (a) [(Meaao)Pd(phen)]Cl, CH$_3$OH AND

TABLE III.1

INFRARED DATA OF $[(Meaao)Pd(L-L)]$ X COMPLEXES IN KBr DISCS (FREQUENCIES ARE IN cm^{-1})

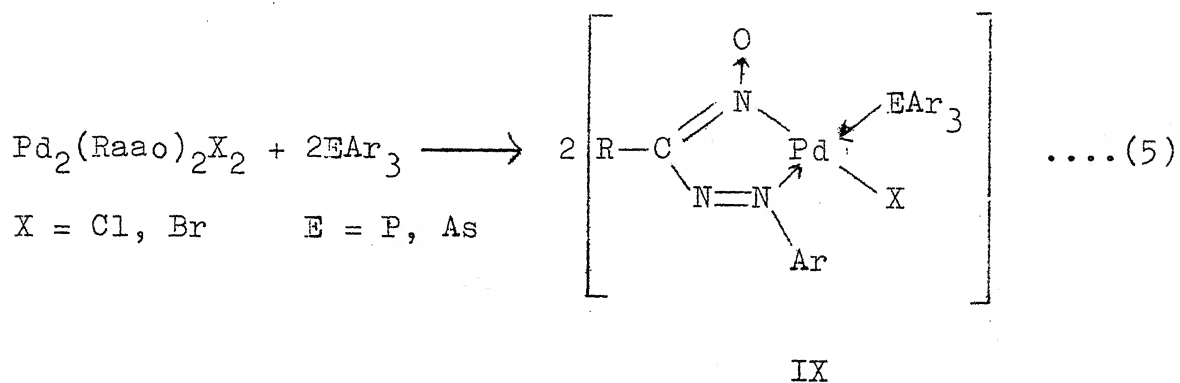| Compound	ν_{C-H}		ν_{N-O}	$\nu_{Cl-O(as)}$ of ClO_4 group[a]	Other vibrations
	R	Ar			
$[(Meaao)Pd(phen)]Cl, CH_3CH$	2940(w)	3060(m)	1270(vs)		O-H 3400 (s, br) phen vibrations: 1620, 1575, 1425, 860 (all s).
$[(Meaao)Pd(en)]Cl$	2940(w)	b	1270(vs)		N-H 3400, 3240, 3065 (all s and br) NH_2 1600 (m, br)
$[(Meaao)Pd(phen)]ClO_4$	2920(w)	3060(m)	1280(vs)	1090(s,br)	phen vibrations: 1620, 1565, 1425, 860 (all s).
$[(Meaao)Pd(en)]ClO_4$	2940(w)	b	1270(vs)	1080(s,br)	N-H 3400, 3240, 3060 (all s and br) NH_2 1590(m).

w = weak; m = medium; s = strong; vs = very strong and br = broad.

a the perchlorate compounds exhibit one strong band at 620 cm^{-1} (asymmetric bend of ClO_4^- group) also.

b not assigned.

C. Reactions with Triphenylarsine and Triarylphosphines

a. The General Reaction

The halo-bridged arylazooximates of palladium(II) undergo extremely facile bridge-splitting reactions with triphenylarsine and triarylphosphines e.g.

$$Pd_2(Raao)_2X_2 + 2EAr_3 \longrightarrow 2\left[\begin{array}{c} \text{IX structure} \end{array}\right] \quad ....(5)$$

X = Cl, Br   E = P, As

IX

The bridge-split products IX are as usual violet crystalline solids which are highly soluble in benzene, chloroform and dichloromethane. The rapidity of the reaction (5) indicates that the bulky EAr_3 ligand in IX most possibly occupies the position <u>trans-</u> to azo-end of the arylazooximato chelate ring.
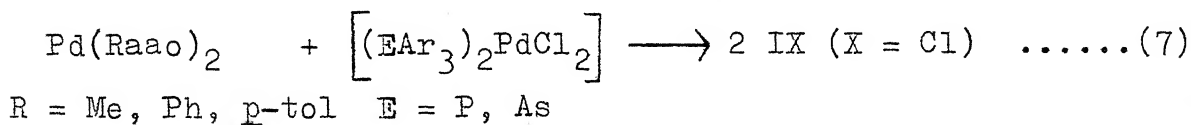
Triphenylarsine, like the N-donor ligands, fails to react further to open the arylazooximato chelate ring even when used in excess. This has been checked by monitoring the intensity of the $\sim$ 500 nm band in the electronic spectra of the bridge-split products IX (E = As, X = Cl or Br) with different ratios of triphenylarsine in benzene. Triaryl-phosphines, to the contrary, react further with IX to yield

open-ring products X and in benzene solution the following
equilibrium exists:

$$\text{IX} \qquad + PAr_3 \rightleftharpoons \qquad \text{X} \qquad \dots\dots(6)$$
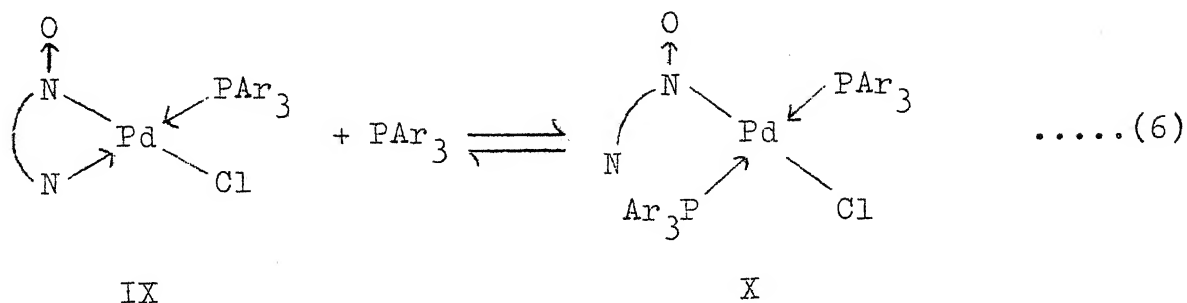
The ring-opening reactions and related equilibrium studies will
be discussed in detail in Chapter IV.

Another interesting method of generating complexes of
the type IX is to mix stoichiometric amounts of bis(arylazo-
oximato)palladium(II) and trans-$\left[(EAr_3)_2 PdCl_2\right]$ in benzene or
chloroform e.g.

$$Pd(Raao)_2 \quad + \left[(EAr_3)_2 PdCl_2\right] \longrightarrow 2 \text{ IX } (X = Cl) \quad \dots\dots(7)$$

R = Me, Ph, p-tol   E = P, As

Reaction (7) is extremely fast and this redistribution of ligand
on two different Pd atoms is really fascinating. Studies on the
detail mechanism of reaction (7) are in progress.

Triarylphosphines readily displace coordinated amine
molecules from $\left[(Raao)Pd(am)X\right]$ complexes. This was confirmed
by the following reactions (with $\left[(Meaao)Pd(am)Cl\right]$ complexes)

which were studied by monitoring the pmr spectra of the reaction mixtures and also by isolating the products from the nmr tube:
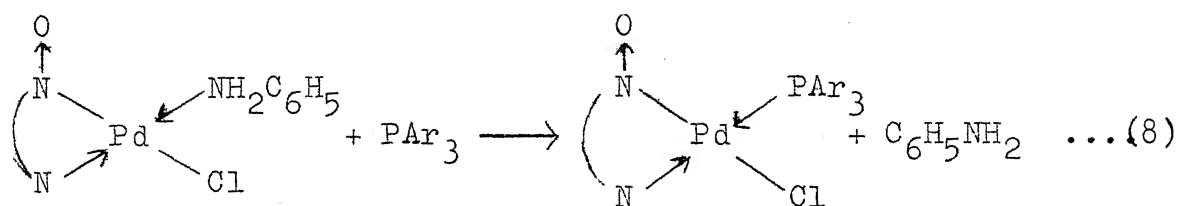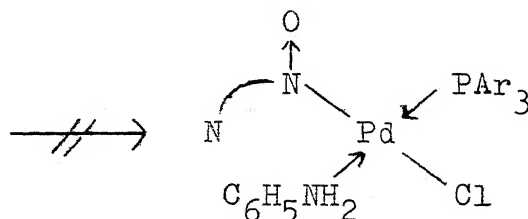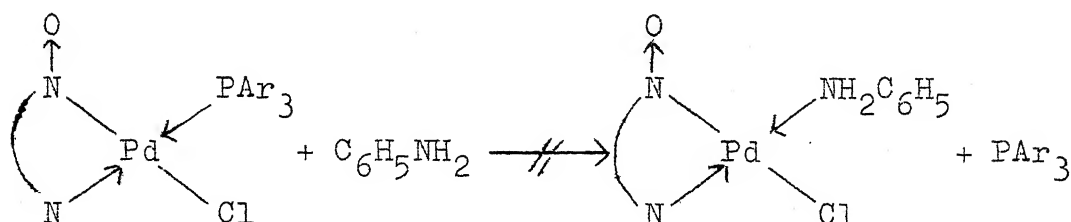

$$\delta_{NH_2} = 5.26 \text{ ppm} \qquad \delta_{NH_2} = 3.66 \text{ ppm}$$
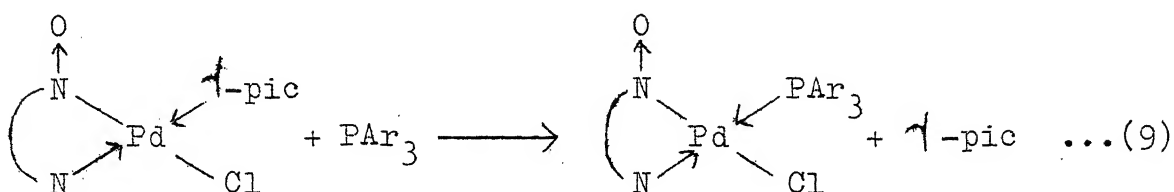
$$\delta_{CH_3}(\gamma\text{-pic}) = 2.38 \text{ ppm} \qquad \delta_{CH_3} = 2.30 \text{ ppm}$$

Thus if a N-donor ligand is already present in the bridge-split product i.e. of the type $\left[(Raao)Pd(am)X\right]$, the

addition of one equivalent of PAr_3 to it results in the preferential displacement of am rather than the opening of arylazooximato chelate ring. The N-donor ligands can neither displace a coordinated PAr_3 molecule nor open the chelate ring.

b. Spectral Data of the Complexes

The electronic spectra of the complexes IX in benzene exhibit the typical intense $\sim$ 500 nm band. The peak positions of the band for different complexes and their extinction coefficients are listed in Table III.8. The infrared data of the complexes IX are set out in Table III.9 and one representative spectrum is shown in Fig. III.7. Strong absorptions at 1480, 1430, 1095, 995 and 510 cm^{-1} all of which are characteristics of coordinated phosphines (or arsine) are present in the spectrum. The 1600-1200 cm^{-1} region of the infrared spectra of complexes IX is in general very much similar to that of $\left[(Raao)Pd(am)X\right]$ complexes (Fig. III.2 and Fig. III.7). This pattern in the infrared spectra of $\left[(Raao)Pd(B)X\right]$ complexes (where B = am or EAr_3) is characteristic of an arylazooximate anion chelated to a palladium atom i.e. of the moiety V. The room temperature pmr spectra of the complexes IX in $CDCl_3$ are all consistent with the compositions proposed and the ^{1}H chemical shifts are set out in Table III.10. The signal for the methyl group of phenylazoacetaldoximato fragment is found to be a little broad for $\left[(Meaao)Pd(EPh_3)X\right]$ E = P or As, complexes but not for $\left[(Meaao)Pd(P(p-tol)_3)X\right]$ complexes (Fig. III.8).

TABLE III.8

ELECTRONIC SPECTRAL DATA OF $\left[(\text{Meaao})\text{Pd}(\text{EAr}_3)\text{Cl}\right]$, (E = P or As) COMPLEXES IN BENZENE AT ROOM TEMPERATURE (λ = BAND MAXIMUM IN nm; ϵ = EXTINCTION COEFFICIENT IN $M^{-1}cm^{-1}$).

Compound	$\lambda(\epsilon)$
$\left[(\text{Meaao})\text{Pd}(\text{PPh}_3)\text{Cl}\right]$	515 (5200)
$\left[(\text{Meaao})\text{Pd}\left(\text{P}(\underline{o}\text{-tol})_3\right)\text{Cl}\right]$[a]	520 (5500)
$\left[(\text{Meaao})\text{Pd}\left(\text{P}(\underline{m}\text{-tol})_3\right)\text{Cl}\right]$[b]	515 (5400)
$\left[(\text{Meaao})\text{Pd}\left(\text{P}(\underline{p}\text{-tol})_3\right)\text{Cl}\right]$[c]	515 (6500)
$\left[(\text{Meaao})\text{Pd}(\text{AsPh}_3)\text{Cl}\right]$	520 (5400)

[a] $\text{P}(\underline{o}\text{-tol})_3$ = tri-$\underline{o}$-tolylphosphine;

[b] $\text{P}(\underline{m}\text{-tol})_3$ = tri-$\underline{m}$-tolylphosphine;

[c] $\text{P}(\underline{p}\text{-tol})_3$ = tri-$\underline{p}$-tolylphosphine.

TABLE 111.2

INFRARED DATA OF $[(Meaao)Pd(EAr_3)X]$ COMPLEXES IN KBr DISCS (FREQUENCIES ARE IN cm^{-1}).

Compound	ν_{C-H} R	ν_{C-H} Ar	ν_{N-O}	ν_{Pd-Cl}	Other Vibrations[a]
$[(Meaao)Pd(PPh_3)Cl]$	2910(w) 2940(w)	3060(m)	1270(vs)	350	1480, 1430, 1095, 995 and 510 (all s)
$[(Meaao)Pd(PPh_3)Br]$	2910(w)	3050(m)	1270(vs)	–	1480, 1430, 1100, 995 and 515 (all s).
$[(Meaao)Pd(P(p-tol)_3)Cl]$	2930(m) 2900(w)	3030(m)	1260(vs)	355	1600, 1500, 1450, 1185, 995, 805 and 530 (all s).
$[(Meaao)Pd(P(p-tol)_3)Br]$	2940(w) 2900(m)	3020(m)	1265(vs)	–	1595, 1490, 1450, 1185, 995, 800 and 520 (all s).
$[(Meaao)Pd(AsPh_3)Cl]$	2920(w)	3040(m)	1270(vs)	345	1480, 1430, 1075, 995 and 460 (all s).

w = weak; m = medium; s = strong and vs = very strong.

a these vibrations are all characteristics of coordinated triaryl phosphines (or arsine).
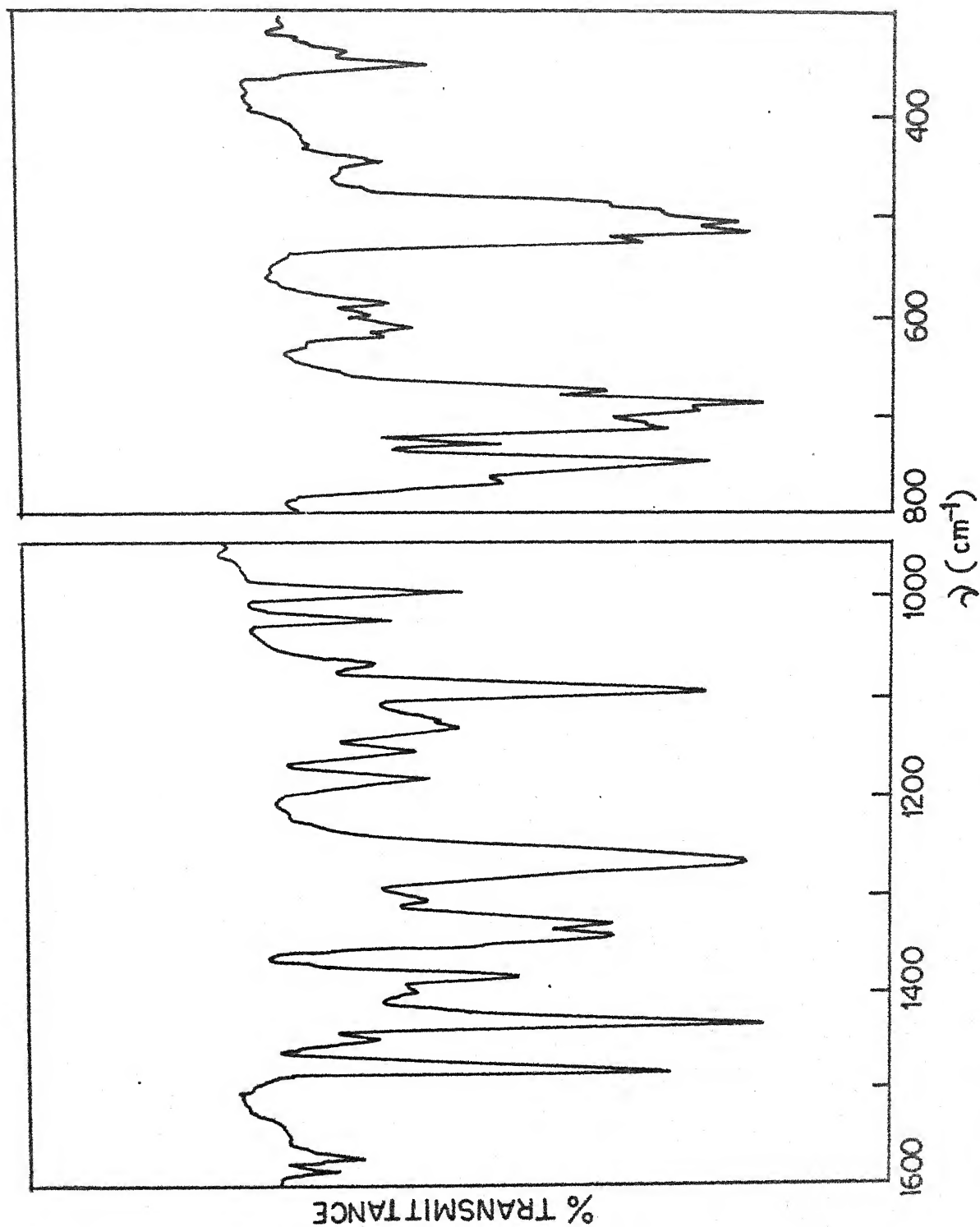
FIG III.7. PARTIAL INFRARED SPECTRUM OF $\left[(Meaao)Pd(PPh_3)Cl\right]$ IN KBr (DISC).

TABLE III.10

^{1}H CHEMICAL SHIFTS^a OF $\left[(Raao)Pd(EAr_3)X\right]$ COMPLEXES

SOLVENT: $CDCl_3$.

Compound	Group	Chemical Shift δ (ppm)
$\left[(Meaao)Pd(PPh_3)Cl\right]$	aao CH_3	2.03 (br)
$\left[(Meaao)Pd(PPh_3)Br\right]$	aao CH_3	2.13
$\left[(Meaao)Pd\left(P(p\text{-tol})_3\right)Cl\right]$	aao CH_3	2.10
	p-CH_3(phosphine)	2.33
$\left[(Meaao)Pd\left(P(ptol)_3Br\right)\right]$	aao CH_3	2.13
	p-CH_3(phosphine)	2.33
$\left[(Meaao)Pd(AsPh_3)Cl\right]$	aao CH_3	2.12 (br)
$\left[(Meaao)Pd(AsPh_3)Br\right]$	aao CH_3	2.13
$\left[(p\text{-tolaao})Pd(PPh_3)Cl\right]$	p-CH_3(aao)	2.23
$\left[(p\text{-tolaao})Pd(PPh_3)Br\right]$	p-CH_3(aao)	2.27

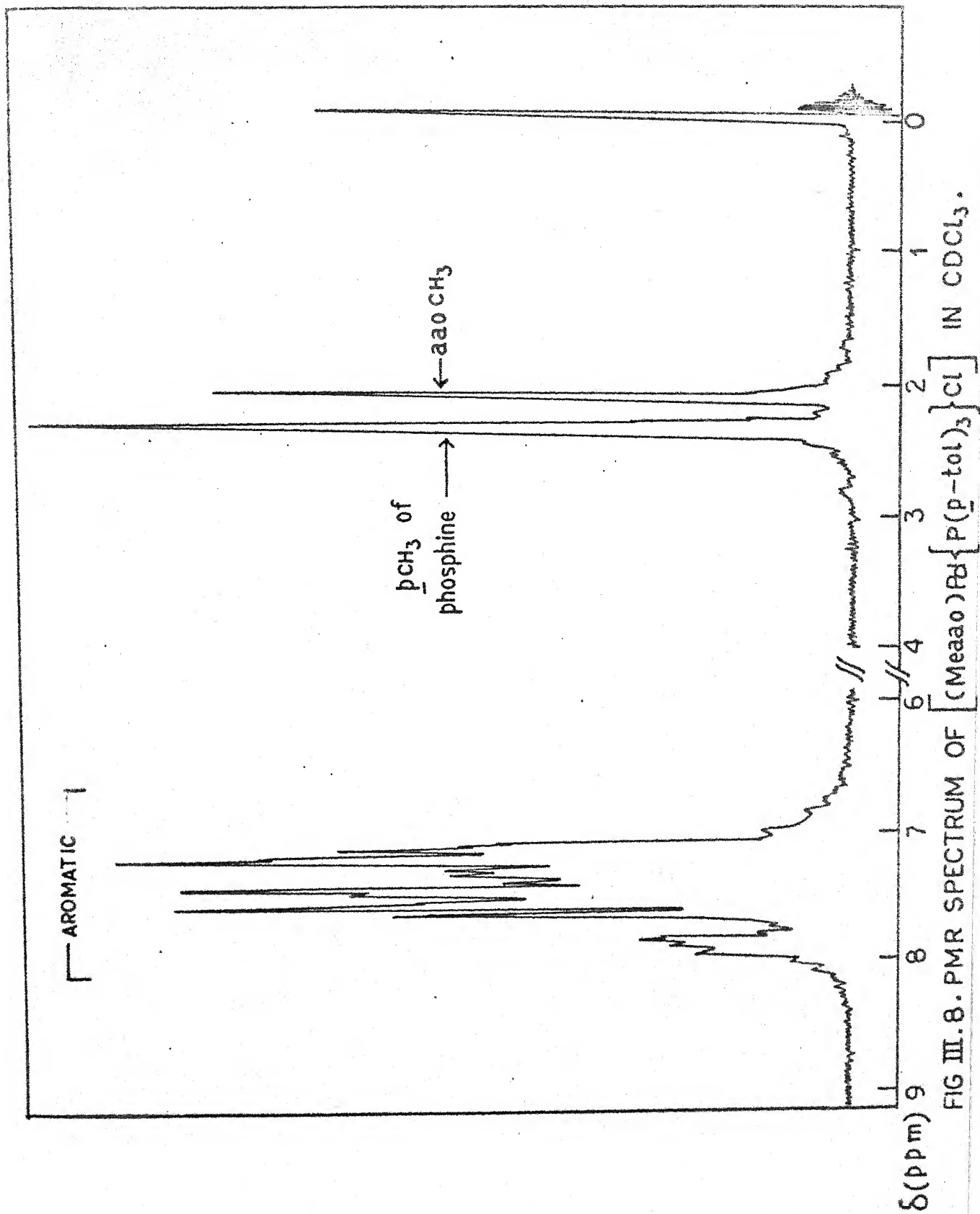^{a} Aromatic protons give signals in the region 6.70-8.50 ppm and are not tabulated; br = broad.

FIG III.8. PMR SPECTRUM OF $[(Meaao)Pd\{P(\underline{p}-tol)_3\}]Cl$ IN $CDCl_3$.

D. Reaction with Cl⁻ ion

The complex $Pd_2(Meaao)_2Cl_2$ dissolves partly in aqueous solution of KCl to give a violet red solution. This observation is an indication that Cl^- ion may cleave the chlorine-bridge (like other Lewis bases) to yield ionic species. The species which immediately suggests itself is $\left[(Meaao)PdCl_2\right]^-$. All attempts to isolate this as the potassium salt from the above solution, however, failed. The next chloride which was tried is $Et_4N^+Cl^-$. $Pd_2(Meaao)_2Cl_2$ does not dissolve completely in an ethanolic solution of stoichiometric amount of $Et_4N^+Cl^-$. Only in presence of excess $Et_4N^+Cl^-$, a clear red solution results. When water is added to this solution, only $Pd_2(Meaao)_2Cl_2$ separates out. In chloroform, $Pd_2(Meaao)_2Cl_2$ reacts with stoichiometric amount of $Et_4N^+Cl^-$ to give a clear red solution but all attempts (including complete evaporation) to isolate the pure ionic species failed. Finally $Ph_4As^+Cl^-$ was tried. $Pd_2(Meaao)_2Cl_2$ reacts with stoichiometric amount of $Ph_4As^+Cl^-$ in dichloromethane to give a clear red solution. Very slow addition of hexane to the concentrated solution leads to deposition of purple crystalline solid of composition $Ph_4As^+\left[(Meaao)PdCl_2\right]^-$. This compound is soluble in acetonitrile, methanol and dichloromethane but insoluble in benzene or hexane. The solution molar electrical conductivity of the complex in acetonitrile (at $30^\circ C$) is 120 $ohm^{-1}cm^2mol^{-1}$. Clearly the complex is an 1:1 electrolyte. The electronic spectrum of the

complex in dichloromethane exhibits an intense band (typical of the moiety V) at 545 nm with an extinction coefficient of 5600. The infrared spectrum of $Ph_4As^+ \left[(Meaao)PdCl_2 \right]^-$ shows two Pd-Cl stretching absorptions (<u>cis</u> configuration) at 330 and 300 cm^{-1}. The complexes <u>cis</u>-$\left[Pd(L)Cl_2 \right]$ where L = $Me_2NCH_2CH_2NMe_2$[24] or $Ph_2NCH_2CH_2NPh_2$[25], exhibit two Pd-Cl stretching frequencies at 330, 321 cm^{-1} and 317, 306 cm^{-1} respectively. The other major vibrations of the complex $Ph_4As^+ \left[(Meaao)PdCl_2 \right]^-$ include ν_{C-H} (phenyl) at 3050 cm^{-1} and ν_{N-O} at 1260 cm^{-1}. Several strong absorptions at 1580, 1480, 1440, 1395, 1345, 1070, 990, 970, 770, 750, 690, 530, 485, 475 and 345 cm^{-1} are also present.

III.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Chemicals

The chemicals and their sources are as follows: Pyridine, aniline, 2,6-lutidine and o-phenanthroline, E. Merck (Germany); ethylenediamine and methylamine (30% aqueous solution) and tetraphenylarsonium chloride, Aldrich Chemical Co. (U.S.A.); -picoline and imidazole, British Drug House Ltd. (England); triarylphosphines, Eastman Organic Chemicals (U.S.A.); triphenylarsine, Alfa Inorganics Inc. (U.S.A.).

Ammonia gas was generated by heating liquor ammonia and dried by allowing the outcoming gas to pass through CaO tubes.

b. The Complexes

(i) The $\left[(Raao)Pd(am)X\right]$ Complexes where am = py, γ-pic, aniline, methylamine or 2,6-lutidine; R = Me, Ph or p-tol and X = Cl or Br

All these complexes were prepared similarly. A typical synthesis (R = Me, X = Cl and am = py) is described below.

To a solution of 183 mg (0.3 mol) of di-μ-chlorobis $\left[phenylazoacetaldoximatopalladium(II)\right]$ in 30 ml of dichloromethane (clear violet solution) was added ∼ 0.2 ml of freshly distilled pyridine. The color changed to purple. The mixture was kept at room temperature for 15 minutes and then the solvent was removed completely on a rotary evaporator. The violet residue thus obtained was recrystallised from benzene. The yield of the violet needles of chlorophenylazoacetaldoximato-pyridinepalladium(II) was ∼ 85%.

Benzene was also used as the solvent for these syntheses. The halo-bridged arylazooximates with R = Ph or p-tol are sparingly soluble in benzene or dichloromethane. The addition of amine, however, increased the solubility in each case and on mild heating the entire solid dissolved to give clear red or purple solution which was finally evaporated in rotary

evaporator.   Since methylamine was used as 30% aqueous solution,
the reaction mixture (i.e. after the addition of amine) was
transferred to another container by careful decantation to avoid
the water drops.

(ii) Amminechlorophenylazoacetaldoximatopalladium(II)

183 mg (0.3 mmol) of di-μ-chlorobis$\left[\text{phenylazoacetald-}\right.$
oximatopalladium(II)$\left.\right]$ was dissolved in 30 ml of dichloromethane.
Through this solution was passed a stream of dry ammonia gas for
1-2 minutes (color changed from violet to purple) and then the
side of the beaker was scratched.   Violet crystalline solid
separated within 10 minutes.   Ammonia gas was passed through
the reaction mixture once (or twice) more (for 10-15 secs)
during this period.   The violet solid was then filtered, washed
with dichloromethane and finally recrystallised from chloroform
(yield $\sim$ 60%).

(iii) Chloroimidazolephenylazoacetaldoximatopalladium(II)

To a solution of 183 mg (0.3 mmol) of di-μ-chlorobis-
$\left[\text{phenylazoacetaldoximatopalladium(II)}\right]$ in 25 ml of dichloromethane
was added with constant stirring a solution of 41 mg (0.6 mmol)
of imidazole in 10 ml of dichloromethane.   The initial violet
color changed to purple.   The mixture was kept at room tempera-
ture for 15 minutes and then the solvent was removed completely
on a rotary evaporator.   The violet solid thus obtained was
recrystallised from benzene (yield $\sim$ 70%).

(iv) Ethylenediaminephenylazoacetaldoximatopalladium(II) chloride

183 mg (0.3 mmol) of di-μ-chlorobis$\Big[$phenylazoacetaldoximatopalladium(II)$\Big]$ was dissolved in 25 ml of dichloromethane. To this solution was added with constant stirring a solution of 36 mg of (0.6 mmol) of ethylenediamine in dichloromethane (a stock solution of known amount of ethylenediamine was prepared and the required volume of solution was used). Immediately violet precipitate appeared. After the addition was complete, the mixture was stirred for 15 minutes and then the solid was filtered, washed with dichloromethane and finally dried in air (yield $\sim$ 70%).

(v) Methanol Adduct of Orthophenanthrolinephenylazoacetaldoximatopalladium(II) Chloride

183 mg (0.3 mmol) of di-μ-chlorobis$\Big[$phenylazoacetaldoximatopalladium(II)$\Big]$ was suspended in 30 ml of methanol and to it was added slowly with stirring a solution of 118 mg (0.6 mmol) of orthophenanthroline monohydrate in 10 ml of methanol. The halo-bridged complex started dissolving as more and more o-phenanthroline was added and finally a clear purple solution resulted. The purple solution was then slowly evaporated under low pressure. When the volume of the solution was reduced to about 1 ml violet crystalline solid started separating out. The solid was filtered, washed with hexane and dried over fused $CaCl_2$ (yield $\sim$ 65%).

(vi) The $[(Raao)Pd(EAr_3)X]$ Complexes where R = Me or p-tol,

X = Cl or Br, E = P or As, Ar = Ph or p-tol

All these complexes were prepared following similar procedure. A typical synthesis (R = Me, X = Cl and EAr_3 = PPh_3) is described below.

To a solution of 304 mg (0.5 mmol) of di-μ-chlorobis [phenylazoacetaldoximatopalladium(II)] in 30 ml of dichloromethane was added with stirring a solution of 262.1 mg (1 mmol) of triphenylphosphine in 20 ml of dichloromethane. As usual the initial violet color changed to purple. The purple solution was then allowed to evaporate slowly (on hot plate). When the volume was about 1 ml, 5 ml of hexane was added very slowly to this concentrated solution. The violet crystalline solid which was deposited was filtered, washed with hexane and finally dried in air (yield $\sim$ 70%).

(vii). Tetraphenylarsonium dichlorophenylazoacetaldoximato-palladate(II)

A solution of 252 mg (0.6 mmol) of tetraphenylarsonium chloride in 10 ml of dichloromethane was added with stirring to a solution of 183 mg (0.3 mmol) of di-μ-chlorobis [phenylazo-acetaldoximatopalladium(II)] in 30 ml of dichloromethane. The initial violet color changed to purple. The solution was then completely evaporated (in rotary evaporator) when a dark purple gum was left. Later the gum was dissolved in minimum amount of

hot benzene-hexane (1:1) mixture and the solution was left in air for slow evaporation. Purple crystalline solid separated within 1 hr. The solid was collected by filtration, washed with hexane and finally dried in air (yield $\sim$ 70%).

(viii) $\left[(\text{Raao})\text{Pd}(\text{EAr}_3)\text{Cl}\right]$ Complexes from $\text{Pd}(\text{Raao})_2$ and trans- $\left[(\text{EAr}_3)_2\text{PdCl}_2\right]$

A typical synthesis (R = Me and EAr_3 = PPh_3) is as follows:

A solution of 130 mg (0.3 mmol) of bis(phenylazoacetald-oximato)palladium(II) in 20 ml of benzene (green in color) was slowly added with stirring, to a solution of 210 mg (0.3 mmol) of trans-bis(triphenylphosphine)palladium(II) chloride in 30 ml of benzene (yellow in color). Immediately the color of the mixture turned violet. After 15 minutes of stirring, the violet solution was slowly concentrated to about 2 ml. 5 ml of hexane was slowly added to this concentrated solution when violet crystalline solid separated. The violet solid was then filtered, washed with hexane and finally dried in air (yield $\sim$ 80%).

B. Characterisation of Complexes

This was done by C, H, N microanalysis and by metal analysis. Characterisation data for the complexes are collected in Table III.11.

CHARACTERISATION DATA OF PALLADIUM(II) COMPLEXES

Compound	MP°C[a]	% C Calc.	% C Found	% H Calc.	% H Found.	% N Calc.	% N Found	% Pd Calc.	% Pd Found
(Meaao)Pd(NH$_3$)Cl]	182	29.91	30.20	3.45	3.62	17.44	17.35	33.15	33.31
(Meaao)Pd(NH$_3$CH$_3$)Cl]	212	32.24	32.51	3.91	3.73	16.71	16.80	31.76	31.82
(Meaao)Pd(NH$_2$C$_6$H$_5$)Cl]	180	42.32	42.20	3.77	3.58	14.10	14.21	26.80	26.64
(Meaao)Pd(py)Cl]	215	40.73	40.81	3.42	3.40	14.62	14.57	27.77	27.30
(Meaao)Pd(γ-pic)Cl]	206	42.31	42.12	3.80	3.68	14.10	14.30	26.80	26.41
(Meaao)Pd(imidazole)Cl]	191	35.48	35.91	3.25	3.40	18.82	18.71	28.60	28.90
(Meaao)Pd(2,6-lutidine)Cl]	153	43.79	44.10	4.17	4.31	13.62	13.48	-	-
(Meaao)Pd(NH$_2$C$_6$H$_5$)Br]	173	38.05	38.03	3.42	3.62	12.68	12.78	24.10	23.91
(Meaao)Pd(py)Br]	197	36.49	36.71	3.06	2.97	13.10	13.32	24.89	25.04
(Meaao)Pd(γ-pic)Br]	195	38.05	38.32	3.42	3.21	12.68	12.64	24.10	24.32
(Phaao)Pd(py)Cl]	b	48.54	48.75	3.39	3.31	12.58	12.71	23.91	24.14
(Phaao)Pd(γ-pic)Cl]	b	49.66	49.82	3.73	3.91	12.20	12.40	-	-
(Phaao)Pd(2,6-lutidine)Cl]	b	50.72	50.64	4.05	3.98	11.83	11.73	-	-
(p-tolaao)Pd(NH$_2$C$_6$H$_5$)Cl]	b	50.73	51.02	4.05	4.12	11.84	11.71	-	-
(p-tolaao)Pd(py)Cl]	b	49.67	49.31	3.73	3.81	12.20	12.12	23.16	23.41
(p-tolaao)Pd(γ-pic)Cl]	b	50.73	50.84	4.05	3.93	11.84	11.95	22.50	22.38

Table III.11 contd..

Compound	MP°C[a]	%C Calc.	%C Found	%H Calc.	%H Found	%N Calc.	%N Found	%Pd Calc.	%Pd Found
[(p-tolaao)Pd(2,6-lutidine)Cl]	b	51.73	51.41	4.34	4.30	11.50	11.70	–	–
[(p-tolaao)Pd(γ-pic)Br]	b	46.37	46.14	3.50	3.81	10.82	11.05	–	–
[(p-tolaao)Pd(2,6-lutidine)Br]	b	47.41	47.61	3.98	3.84	10.53	10.70	–	–
(Meaao)Pd(pnen)]Cl, CH₃OH	145	48.83	48.90	3.90	3.78	13.56	13.27	20.61	20.60
(Meaao)Pd(en)]Cl	270	32.96	32.31	4.47	4.21	19.23	19.10	–	–
(Meaao)Pd(phen)]ClO₄	264	43.80	43.72	2.94	3.02	12.77	12.58	–	–
(Meaao)Pd(en)]ClO₄	–	28.03	27.97	3.77	3.89	16.35	16.43	–	–
(Meaao)Pd(PPh₃)Cl	187	55.12	55.42	4.10	3.98	7.42	7.51	19.54	19.31
(Meaao)Pd(PPh₃)Br	175	51.10	51.34	3.79	3.70	6.88	6.87	17.44	17.36
(Meaao)Pd(P(p-tol)₃)Cl	c	57.23	57.37	4.80	4.72	6.90	7.01	17.47	17.60
(Meaao)Pd(P(p-tol)₃)Br	c	53.33	53.21	4.48	4.51	6.43	6.41	–	–
(Meaao)Pd(AsPh₃)Cl	246	51.15	51.30	3.80	3.71	6.88	6.73	17.44	17.51
Ph₄As[(Meaao)PdCl₂]	c	53.13	53.30	3.90	3.78	5.81	5.81	14.72	14.82

a. All melting points reported in this table are uncorrected; b The compound loses 'amine' around 200°C to yield the halo-bridged arylazooximate which does not melt below 280°C; c The compound melts over a wide range of temperature with decomposition.

C. Physical Measurements

a. Infrared Spectra

Details are given in Chapter II. In the region 500-250 cm^{-1}, spectra were recorded in nujol mull using polyethylene windows.

b. Electronic Spectra

Details are given in Chapter II.

c. Electrical Conductance Measurements

These were measured on a Systronics (India) Conductivity Bridge using a conductivity cell with platinised platinum electrode system of cell constant = 0.548 cm^{-1}. Spectroscopic quality methanol was used. Acetonitrile was purified following standard procedure[26].

d. Proton Resonance Measurements

Details are given in Chapter II.

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CHAPTER IV

RING-OPENING REACTIONS OF
DI-μ- HALOBIS $\left[\text{ARYLAZOOXIMATOPALLADIUM(II)}\right]$

CHAPTER IV

RING-OPENING REACTIONS OF

DI-μ- HALOBIS $\left[\text{ARYLAZOOXIMATOPALLADIUM(II)}\right]$

Abstract: The arylazooximato (aao) chelate ring is opened at
the azo-end by triarylphosphines (PAr$_3$). PAr$_3$ reacts with
$\left[\text{(Meaao)Pd(PAr}_3\text{)X}\right]$ to produce $\left[\text{(Meaao)Pd(PAr}_3\text{)}_2\text{X}\right]$ in which
the aao fragment is monodentate (linked to Pd atom through the
oxime-end only) in solid state. The opening of the aao chelate
ring is characterised by the disappearance of the $\sim$ 500 nm band
in the electronic spectrum and the appearance of new infrared
absorption at $\sim$ 1490 cm^{-1}. In $\left[\text{(Meaao)Pd(PAr}_3\text{)}_2\text{X}\right]$, the two
PAr$_3$ molecules are trans- to each other. In the room temperature
pmr spectrum of $\left[\text{(Meaao)Pd(PAr}_3\text{)}_2\text{X}\right]$, the methyl signal appears
at an unusually high-field region (δ = 0.87 ppm) which is
believed to be due to diamagnetic shielding of the methyl group
by the phenyl groups of the phosphine. In solution, the
$\left[\text{(Meaao)Pd(PAr}_3\text{)}_2\text{X}\right]$ complexes are in equilibrium with
$\left[\text{(Meaao)Pd(PAr}_3\text{)X}\right]$ and PAr$_3$. The constants for the equilibrium
with various triarylphosphines have been determined by spectro-
scopic technique. The observed values of the equilibrium
constants parallel the basicities (of the phosphines) expected
from cone angle considerations. Both tri-o-tolylphosphine and

triphenylarsine are unable to open the aao chelate ring due to steric reason and weak basicity of the As center respectively. The 1:2 reaction between $Pd_2(Meaao)_2X_2$ and $Ph_2PCH_2CH_2PPh_2$ (diphos) or $Ph_2PCH_2CH_2AsPh_2$ (arphos) leads to the formation of $[(Meaao)Pd(diphos)X]$ or $[(Meaao)Pd(arphos)X]$. The aao fragment in these species remains in the open-azo configuration both in solid state and in solution. $Pd_2(Meaao)_2X_2$ reacts with one equivalent of diphos (or arphos) to produce $Pd(Meaao)_2$ and $(diphos)PdX_2$ (or $(arphos)PdX_2$). The 2:1 reaction between $[(Meaao)Pd(diphos)X]$ (or $[(Meaao)Pd(arphos)X]$ and $Pd_2(Meaao)_2X_2$ also yields $Pd(Meaao)_2$ and $(diphos)PdX_2$ (or $(arphos)PdX_2$).

Introduction of dry HCl gas into solution of $Pd_2(Raao)_2Cl_2$ in benzene opens the aao chelate rings with concomitant protonation of the oximato groups resulting in the formation of $Pd_2(HRaao)_2Cl_4$. In $Pd_2(HRaao)_2Cl_4$, the aao fragments are believed to be bound to Pd atom through the azo-end. The complexes are quite unstable and are rapidly converted to $Pd_2(Raao)_2Cl_2$ by evolving HCl. $Pd_2(HRaao)_2Cl_4$ (R = Me,Ph) exhibit broad ν_{O-H} and $\nu_{Pd-Cl(terminal)}$ at ~ 3100 cm^{-1} and ~ 350 cm^{-1} respectively. Addition of PPh_3 to solution of $Pd_2(HRaao)_2Cl_4$ in benzene produces trans-$[(PPh_3)_2PdCl_2]$. Passage of HCl gas through solution of $[(Meaao)Pd(PPh_3)_2Cl]$ in benzene also yields trans-$[(PPh_3)_2PdCl_2]$. Thus by the successive use of PAr_3 and HCl (in any order), the entire chelated arylazooximato fragment can be taken off from the Pd atom.

IV.1 <u>INTRODUCTION</u>

This chapter concerns the generation and characterisation of some palladium(II) complexes where an arylazooximato fragment (abbreviated hereafter as aao fragment) is linked to the metal center through one end only. Two types of species are possible; first, in which the aao fragment is bound to the palladium atom through the oxime-end (open-azo species) and second in which the aao fragment is attached to the palladium atom through the azo-end (open-oxime species). Both the types of species have been generated starting from the chelated species I. The strategy adopted was to open the aao chelate

$$\left[\; R\!-\!C \begin{matrix} N\!=\!N \\ \\ N \\ \downarrow \\ O \end{matrix} \begin{matrix} Ar \\ \\ Pd \end{matrix} \diagdown X \;\right]_2$$
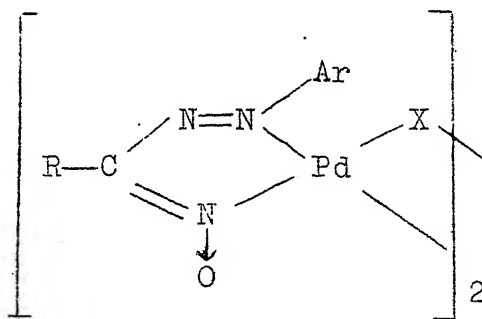
I

ring selectively at the required end by suitable reagent. The results of the ring-opening reactions constitute the subject matter of this chapter.

IV.2 RESULTS AND DISCUSSION

A. Opening at the Azo-end

Opening at the azo-end of an aao chelate ring can be brought about by reaction with phosphines.

a. Reaction with Monodentate Phosphines

The reaction of monodentate phosphines with II is as follows:

$$\text{II} + PAr_3 \rightleftharpoons \text{III} \qquad \dots (1)$$

II   III
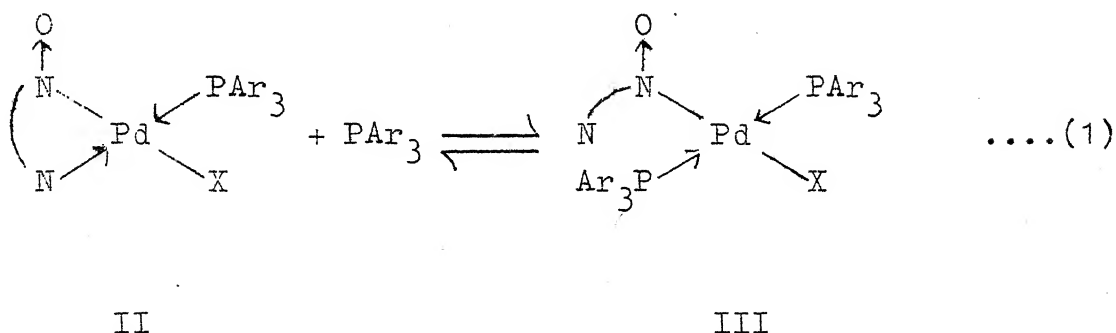
Generation of II from the halo-bridged complex I is already described in Chapter III. Because of solubility problem, the major part of the investigation was confined to arylazooximates with R = Me only. Other arylazooximates (with R different from Me) have been studied in a few isolated cases.

When II (R=Me) is allowed to react with two equivalents of PAr_3 in benzene or dichloromethane and the reaction mixture is concentrated to a small volume, III separates out as bright

orange crystalline solid. We will discuss the nature of the complex III with Ar = Ph and X = Cl in detail. The complex $\left[(\text{Meaao})\text{Pd}(\text{PPh}_3)_2\text{Cl}\right]$ is a bright orange crystalline solid which exhibits an electronic band at 465 nm in solid state. It however, dissolves in benzene, chloroform or dichloromethane to give red solution . In benzene solution, bands at 515, 430 and 330 nm are observed (Fig. IV.1). The 515 nm band is clearly due to the closed-ring species (i.e.II). The intensity of this band increases with dilution and the whole spectrum of $\left[(\text{Meaao})\text{Pd}(\text{PPh}_3)_2\text{Cl}\right]$ approaches that of II (Ar = Ph, X = Cl). Addition of PPh_3 brings about a reverse effect. These observations suggest that in solution III is in dynamic equilibrium with II and PAr_3 as indicated in reaction (1). The constants for the equilibrium(1) with different arylphosphines have been determined. Details are given in section IV.2.A.b. That the reaction of II with PAr_3 does not lead to the ionic species IV is evident from (i) the disappearance of the 515 nm band in the

$$\left[\begin{array}{c} O \\ \uparrow \\ N \\ \diagdown \\ \quad Pd \diagup^{PAr_3} \\ N \diagup \quad \diagdown_{PAr_3} \end{array}\right]^{+} X^{-}$$

IV
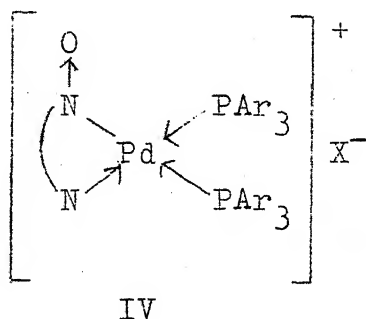
adduct and (ii) the lack of change in solution conductivity (nitromethane solution) on progressive addition of PAr_3 to II.
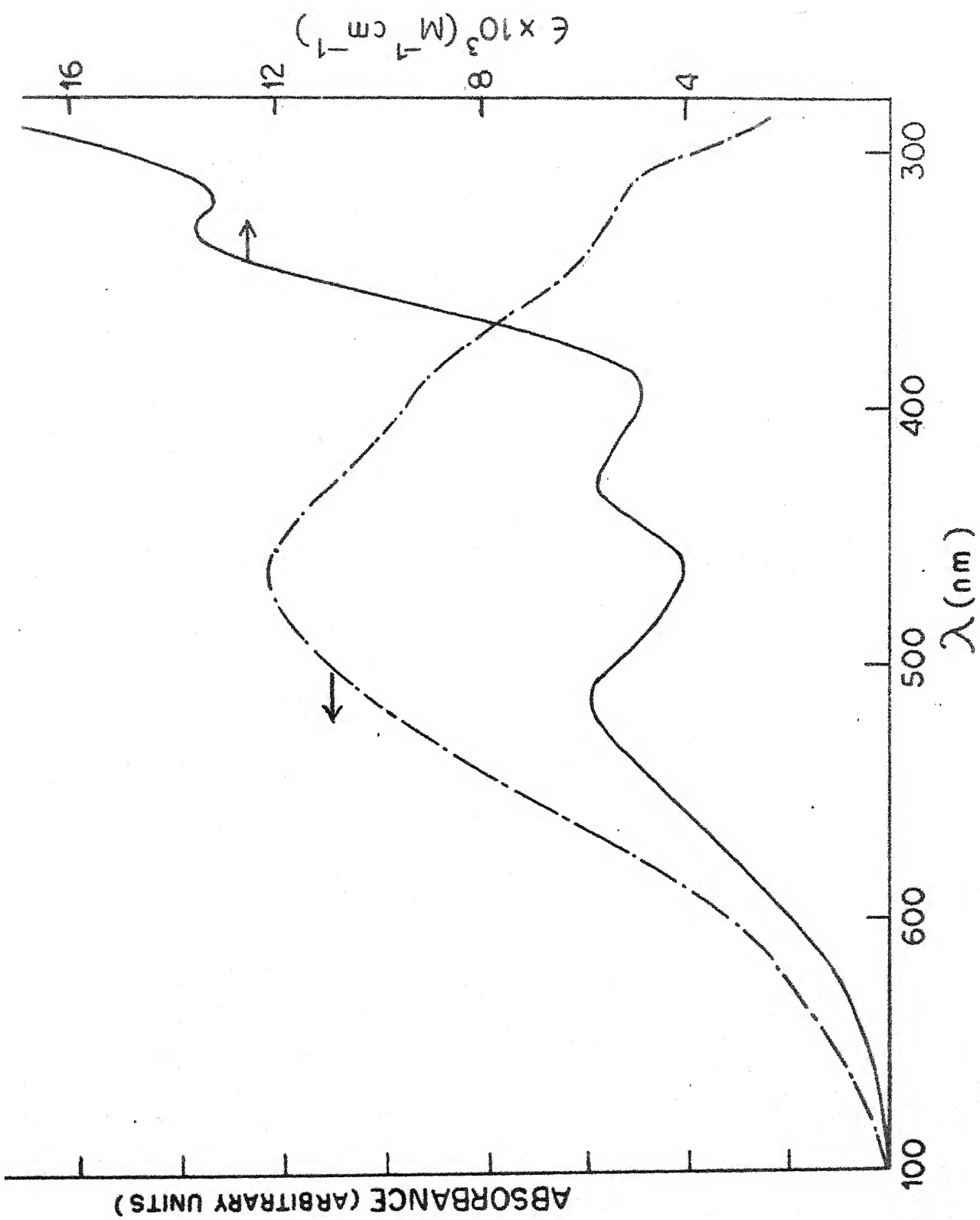
FIG. IV.1. ELECTRONIC SPECTRA OF $\left[(Meaao)Pd(PPh_3)_2Cl\right]$ IN

The infrared spectrum of $[(Meaao)Pd(PPh_3)_2Cl]$ exhibits strong bands at 1480, 1435, 1095, 995 and 510 cm^{-1} (Table IV.4) which are also characteristic PPh$_3$ vibrations of trans- $[(PPh_3)_2PdCl_2]$. Opening of the azo-end (labilised by the trans- PPh$_3$) in II naturally leads to a trans- disposition of the two PPh$_3$ molecules in III. It is believed that $[(Meaao)Pd(PPh_3)_2Cl]$ has the two PPh$_3$ ligands in trans-configuration as in trans- $[(PPh_3)_2PdCl_2]$. Some Pd(II) complexes of para-substituted aryl(tertiary phosphines)[1] $(4-ZC_6H_4)_n P(CH_3)_{3-n}$, n = 1,2 and Z = Cl, H, CH$_3$, exist in the cis- form in solid state but spontaneously isomerize to equilibrium mixtures of cis- and trans- isomers in solution (pmr data). In the case of $[(Meaao)Pd(PPh_3)_2Cl]$ only one form, presumably the trans- form exists in CDCl$_3$ solution (vide infra).

The opening of the aao chelate ring at the azo-end brings about a definite change in the infrared spectra of the aao species (Fig.IV.2). New absorption around 1490 cm^{-1} appears whenever the azo-end of the aao chelate ring is open (Fig.IV.2 and also Chapter V). Opening of the azo-end of chelate rings by excess[2] or stoichiometric amount[3] of phosphine is reported for a few halo-bridged cyclopalladated complexes. In the open-ring products, the two PPh$_3$ ligands are trans- to each other[2]. The aao system is particularly interesting because of the fact that no M-C σ-bond is involved. In $[(Meaao)Pd(PPh_3)_2Cl]$, ν_{Pd-Cl} appears at 335 cm^{-1} (in II ν_{Pd-Cl} is at 350 cm^{-1}).
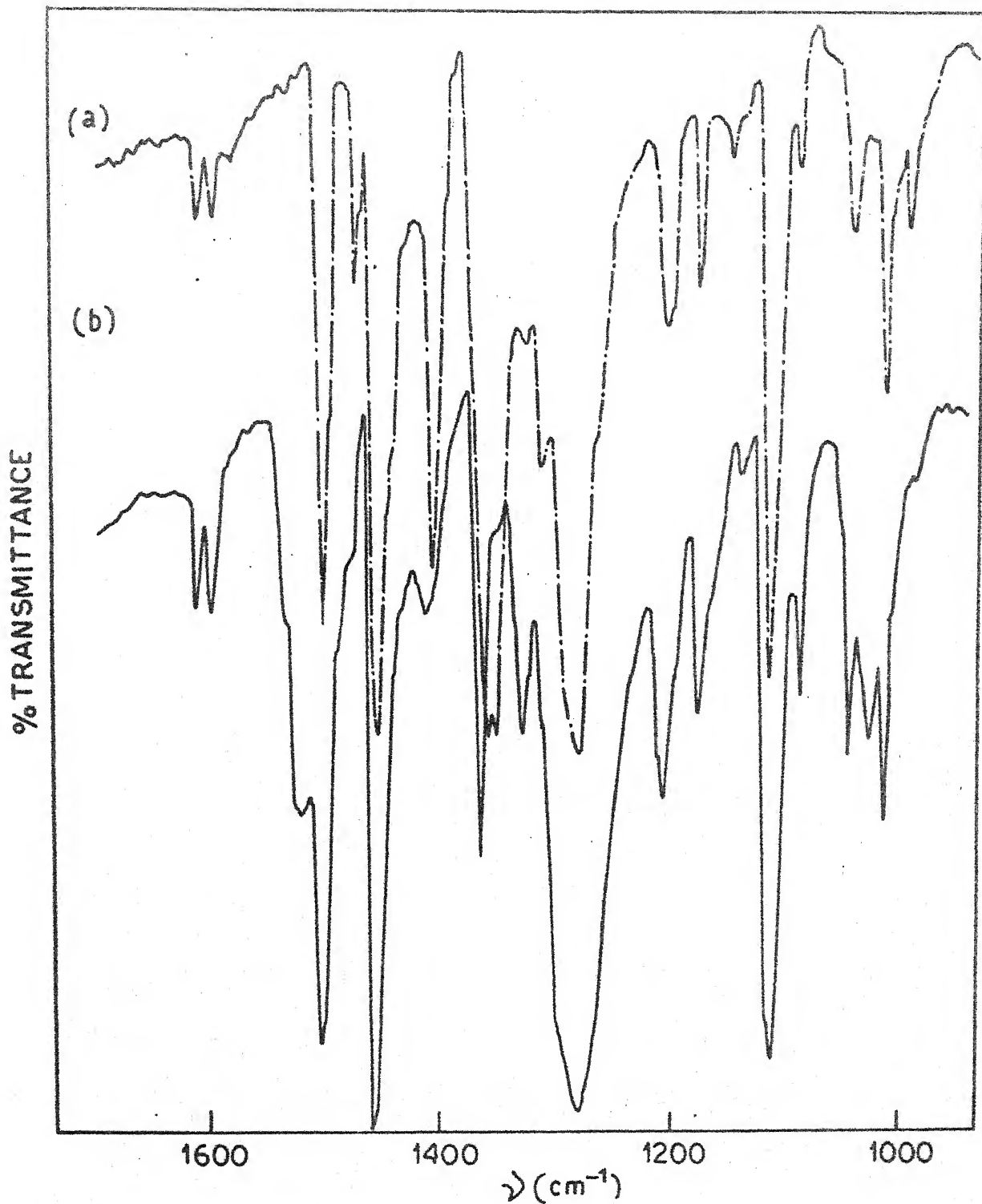
FIG $\overline{\text{IV}}$. 2. PARTIAL INFRARED SPECTRA OF (a) $\left[\text{(Meaao)Pd(PPh}_3\text{)Cl}\right]$ AND (b) $\left[\text{(Meaao)Pd (PPh}_3\text{)}_2\text{Cl}\right]$ IN KBr(DISC).

The compound <u>trans</u>- $\left[(PPh_3)_2PdCl_2\right]$ exhibits[4] ν_{Pd-Cl} at 357 cm^{-1} and in complexes of the type $\left[(N-C)Pd(PPh_3)_2Cl\right]$ where C–N is a ligand bound to palladium through M–C σ-bond, ν_{Pd-Cl} frequencies usually appear at a relatively lower energy region[3,5] viz 320–280 cm^{-1}. The oximato group seems to have an in-between <u>trans</u>-labilising effect.

Reaction (1) was followed by monitoring the pmr spectra of reaction mixtures containing different ratios of $Pd_2(Meaao)_2Cl_2$ and PPh_3. The spectra are displayed in Fig. IV.3. The broad methyl signal of the aao chelate ring in II at δ = 2.03 ppm (generated <u>in situ</u> when $Pd_2(Meaao)_2Cl_2$: PPh_3 = 1:2) slowly moves to the higher field side as more and more PPh_3 is added. Though both II and III are involved in equilibrium(1), only one broad signal is always recorded which is a weighted average of the two methyl signals corresponding to the closed-ring and open-ring species. This observation points to the fact that in $CDCl_3$ the interconversion rate in equilibrium(1) at room temperature is fast by pmr time scale. Finally when $Pd_2(Meaao)_2Cl_2$: PPh_3 = 1:4 (i.e. when a high concentration of III is expected in the nmr tube) we get a sharp methyl signal at an unusually high field viz δ = 0.87 ppm. This spectrum is the limiting one and no further change is observed with the addition of more PPh_3. The same methyl signal is recorded for $\left[(Meaao)Pd(PPh_3)_2Br\right]$ and $\left[(Meaao)Pd\left(P(\underline{p}\text{-tol})_3\right)_2Cl\right]$. The methyl group of the aao fragment in III seems to be in a highly shielded environment. This is quite possible if the methyl

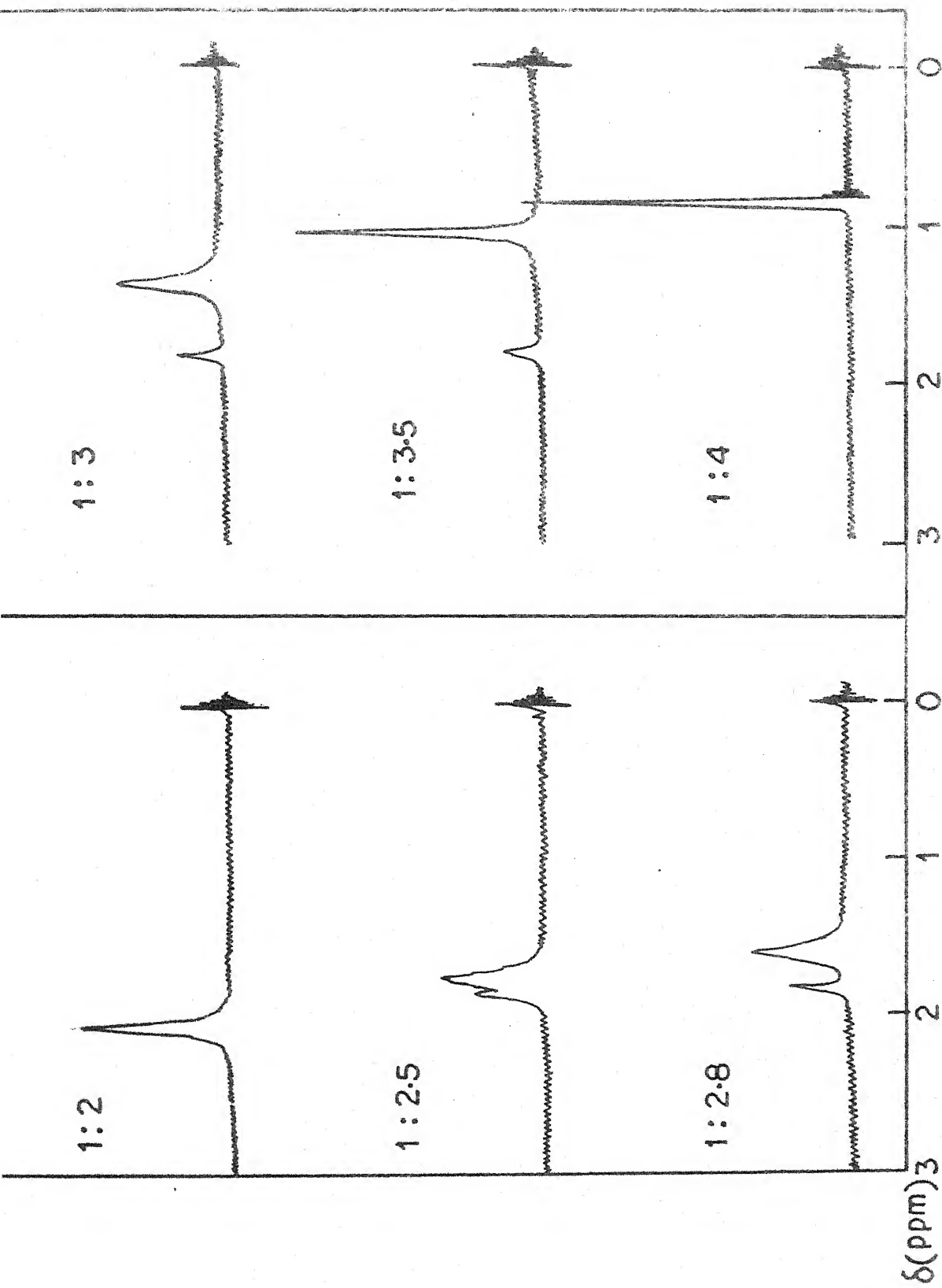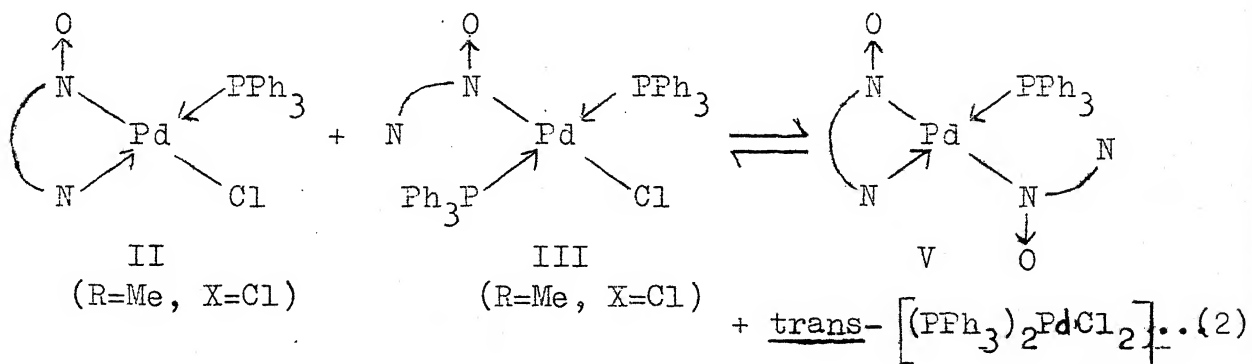FIG IV. 3. PMR SPECTRA OF MIXTURES OF $Pd_2(Meaao)_2Cl_2$ AND TRIPHENYL-PHOSPHINE (PPh_3). THE MOLE RATIO OF $Pd_2(Meaao)_2Cl_2$ AND PPh_3 IS SHOWN

group in III is oriented in such a fashion that it lies in the shielding cones of the phenyl rings of triarylphosphine. Aniso-**tropic** shielding effect of PPh_3 ligand on nearby methyl group in square-planar complexes of palladium[6] and platinum[7] has been reported. However, in no case the effect is so dramatic as in the case of III. High-field shift of a lesser magnitude is also observed when the aao chelate ring is opened at the azo-end by bidentate phosphines (<u>vide infra</u>).

A close look at Fig. IV.3 reveals the appearance of one weak signal at δ = 1.82 ppm when $Pd_2(Meaao)_2Cl_2$:PPh_3 reaches the value 1:2.5. This signal persists through the next few successive additions of PPh_3 but its intensity diminishes slowly and it vanishes completely when $Pd_2(Meaao)_2Cl_2$: PPh_3 = 1:4. This weak signal has been identified to be originating from the species V (Chapter V) which is generated in the reaction (2).

$$
\begin{array}{ccc}
\text{II} & \text{III} & \text{V} \\
(R=Me,\ X=Cl) & (R=Me,\ X=Cl) &
\end{array}
$$

$$+ \ \underline{trans} - \left[(PPh_3)_2 PdCl_2\right]..(2)$$

This reaction is analogous to the reversal of the synthetic reaction (7) in Chapter III. Thus the addition of

PPh$_3$ to II mainly brings about the opening of the aao chelate ring but this reaction is also accompanied by another parallel reaction (2). When sufficient PPh$_3$ has been added to deplete the solution of II, reaction (2) is reversed yielding III as the sole final product of the reaction between II and PPh$_3$. The fact that a separate methyl signal (different from the methyl signals of II and III) is recorded for V, indicates that the equilibrium (2) is slow by pmr time scale.

b. Equilibrium Constants

As stated earlier, a concentrated solution (orange) of III in benzene turns red on dilution due to dissociation to II and PAr$_3$ (equilibrium (1)). Addition of PAr$_3$ to the red solution bleaches the red color by increasing the concentration of III. An isosbestic point is observed on progressive addition of PAr$_3$ (Fig. IV.4). The equilibrium constants for (1) with various aryl phosphines were determined spectroscopically using the intensity of the 510 nm band as a measure of the closed-ring species II (III and PAr$_3$ are transparent in this region). A solution of known concentration of II (or III) R = Me, X= Cl, in benzene was taken and the intensity of the 515 nm band (actually the point of observation was 550 nm to avoid intensity overlap from the strong band at 430 nm) was monitored with different ratios of the phosphines (triphenylphosphine, tri-m-tolylphosphine and tri-p-tolylphosphine).

x = Total concentration of palladium species.

y = Concentration of PPh$_3$ externally added.

Curve a : x = 0·483 × 10^{-4}M;
b : x = 0·473 × 10^{-4}M; y = 0·745 × 10^{-4}M;
c : x = 0·455 × 10^{-4}M, y = 2·165 × 10^{-4}M;
d : x = 0·473 × 10^{-4}M, y = 7·480 × 10^{-4}M;
e : x = 0·464 × 10^{-4}M, y = 14·674 × 10^{-4}M;
f : x = 0·439 × 10^{-4}M, y = 34·684 × 10^{-4}M.
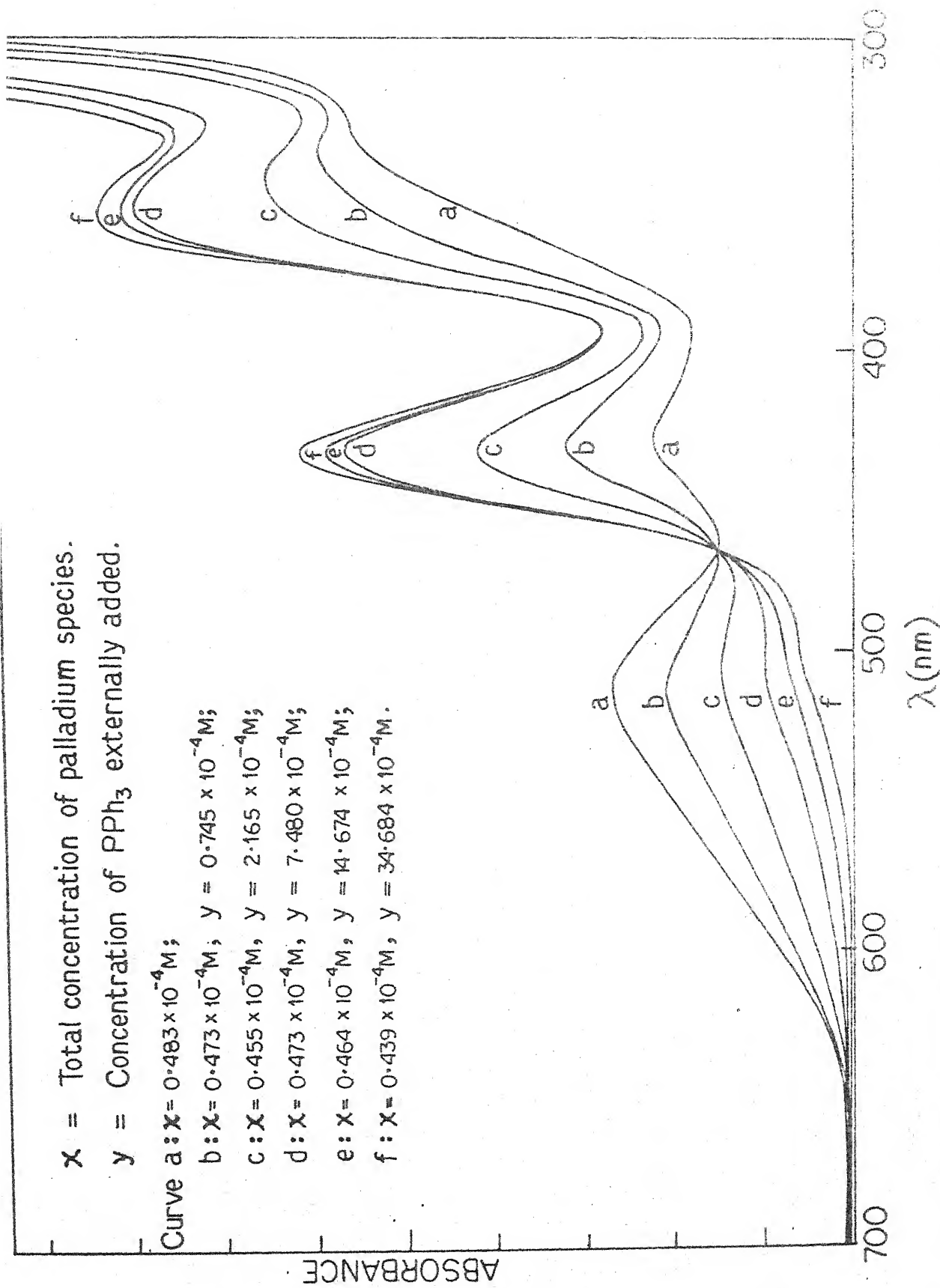
FIG. IV. 4 ELECTRONIC SPECTRA OF EQUILIBRIUM MIXTURES OF II (Ar = Ph, X = Cl) AND III (Ar = Ph, X = Cl) IN BENZENE AT 25°C

The equilibrium constant K for reaction (1) is

$$K = \frac{\left[\text{open-ring species}\right]}{\left[\text{closed-ring species}\right]\left[\text{free } PAr_3\right]}$$

In the case of triphenylphosphine the experiment was conducted by mixing various concentrations of the donor with a solution containing known amount of III. In this case.

$$K = \frac{a}{\left[(a_0-a)\right]\left[b_0+(a_0-a)\right]} \qquad \ldots\ldots\ldots(3)$$

where

a_0 = total concentration of palladium species (II + III)

b_0 = concentration of PPh_3 externally added

a = equilibrium concentration of open-ring species (III)

$\left(a_0-a\right)$ = equilibrium concentration of closed-ring species (II)

and

$b_0 + (a_0-a)$ = equilibrium concentration of free PPh_3.

The quantity (a_0-a) is given by

$$a_0 - \alpha = \frac{A}{\epsilon} \qquad \ldots\ldots\ldots(4)$$

where A is the absorbance (1 cm path length) of the equilibrium mixture at 550 nm and ϵ is the extinction coefficient of II at 550 nm. Since a_0 and b_0 are known and (a_0-a) is determined as above (ϵ_{550} of II with Ar = Ph, X = Cl is 4020), K is readily calculated. Results are shown in Table IV.1.

It should be noted here that while deriving the
expression for K, no concentration term for the species V has
been included. The species V has been neglected since it is
formed only in the initial stages of the reaction between II and
PAr_3 (upto II : PAr_3 = 1:1) and that too its concentration
is always small compared to that of III (pmr data). Hence the
exclusion of the concentration term for the species V from
the expression for K may not introduce much error.

In the cases of tri-m-tolylphosphine and tri-p-tolyl-
phosphine, the experiments were conducted by adding various
concentrations of the phosphines to solutions of II of known
concentration. In these cases

$$K = \frac{a}{(a_o-a)(b_o-a)} \qquad\qquad \ldots\ldots\ldots(5)$$

where

a_o = concentration of closed-ring species II taken

(a_o-a) = equilibrium concentration of closed-ring species II

a = equilibrium concentration of open-ring species III

b_o = concentration of phosphine externally added

and

(b_o-a) = equilibrium concentration of free phosphine.

Since a_o and b_o are known quantities and (a_o-a) can be
determined with the help of equation (4), values of K are
readily calculated. The extinction coefficients at 550 nm,
ϵ_{550} of $\left[(Meaao)Pd\left(P(\underline{m}\text{-tol})_3\right)Cl\right]$ and $\left[(Meaao)Pd\left(P(\underline{p}\text{-tol})_3\right)Cl\right]$

are 3800 and 4900 respectively. The results of these experiments are collected in Table IV.2 and IV.3.

Behavior of Tri-o-tolylphosphine and Triphenylarsine

It is interesting to note that though tri-o-tolylphosphine splits the halogen-bridge in I to yield complexes of the type II, it fails to open the aao chelate ring in II to produce III even when used in excess. No change in the electronic spectrum of II is observed with progressive addition of tri-o-tolylphosphine. This behavior can most possibly be attributed to steric hindrance. The pronounced decrease in basicity (towards proton) of ortho-substituted arylphosphines due to steric crowding has been reported by Kolling and Mawdsley[8].

Like tri-o-tolylphosphine, triphenylarsine cleaves the halogen-bridge in I (producing II) but is unable to open the aao chelate ring in II (spectral data). This inability is due to inherent weak basicity of triphenylarsine as evident from the pK_b data[8]: triphenylphosphine, 8.57; tri-o-tolylphosphine, 9.28 and triphenylarsine, 10.60.

Rationalisation of Equilibrium Data

It has long been recognised that changing substituents on phosphorus ligands can cause marked changes in the behavior

EQUILIBRIUM CONSTANT DATA (AT 25°C) FOR THE REACTION

$$\left[(Meaao)Pd(PPh_3)Cl\right] + PPh_3 \rightleftharpoons \left[(Meaao)Pd(PPh_3)_2Cl\right]$$

a_o (x 10^{-4} M)	b_o (x 10^{-4} M)	A	$(a_o-a) = \dfrac{A}{\epsilon}$ (x 10^{-4} M)	a (x 10^{-4} M)	$b_o + (a_o-a)$ (x 10^{-4} M)	$10^3 K$
	1.526	0.35	0.870	0.570	2.396	2.7
	3.053	0.28	0.696	0.744	3.749	2.9
	6.106	0.21	0.522	0.918	6.628	2.7
1.440	9.157	0.16	0.398	1.042	9.555	2.7
	12.210	0.13	0.323	1.117	12.533	2.8
	15.261	0.11	0.273	1.167	15.534	2.8

Ave: 2.8

EQUILIBRIUM CONSTANT DATA (AT 25°C) FOR THE REACTION

$$\left[(\text{Meaao})Id\left(P(\underline{m}\text{-tol})_3\right)Cl \right] + P(\underline{m}\text{-tol})_3 \rightleftharpoons \left[(\text{Meaao})Pd\left(P(\underline{m}\text{-tol})_3\right)_2\right)Cl \right]$$
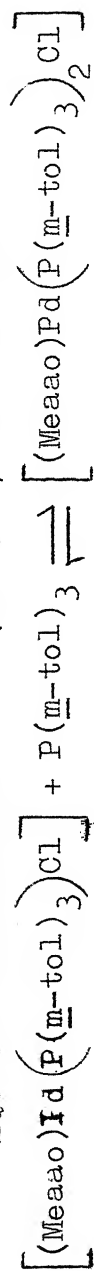
a_o (x 10^{-4} M)	b_o (x 10^{-4} M)	A	$(a_o-a) = \dfrac{A}{\varepsilon}$ (x 10^{-4} M)	a (x 10^{-4} M)	(b_o-a) (x 10^{-4} M)	10^3K
1.00	0.50	0.29	0.76	0.24	0.26	12.1
	1.00	0.22	0.58	0.42	0.58	12.5
	1.50	0.17	0.46	0.54	0.96	12.2
	2.00	0.14	0.37	0.63	1.37	12.4
	2.50	0.12	0.31	0.69	1.81	12.3
	3.00	0.10	0.26	0.74	2.26	12.6

Ave: 12.4

TABLE IV.3

EQUILIBRIUM CONSTANT DATA (AT 25°C) FOR THE REACTION

$$\left[(Meaao)Pd\left(P(\underline{p}\text{-tol})_3\right)Cl\right] + P(\underline{p}\text{-tol})_3 \rightleftharpoons \left[(Meaao)Pd\left(P(\underline{p}\text{-tol})_3\right)_2\right]Cl$$
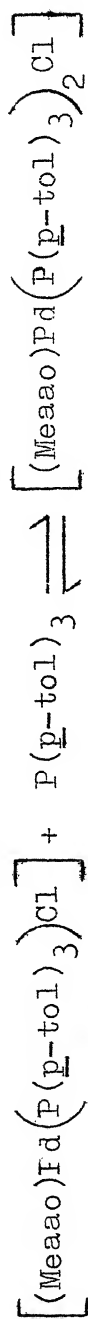
a_o ($\times 10^{-4}$ M)	b_o ($\times 10^{-4}$ M)	A	$(a_o-a)=\frac{A}{\epsilon}$ ($\times 10^{-4}$ M)	a ($\times 10^{-4}$ M)	(b_o-a) ($\times 10^{-4}$ M)	10^3K
1.00	1.00	0.30	0.67	0.33	0.67	7.3
	1.50	0.28	0.57	0.43	1.07	7.0
	2.00	0.24	0.49	0.51	1.49	7.0
	2.50	0.21	0.43	0.57	1.93	6.9
	3.00	0.18	0.37	0.63	2.37	7.1
	3.50	0.17	0.34	0.66	2.84	6.9
	4.00	0.15	0.30	0.70	3.30	7.1
	4.50	0.13	0.27	0.73	3.77	7.1

Ave: 7.1

of the free ligands and their transition metal complexes.
Therefore, rationalisations of the observed behaviors of the
compounds have been attempted mostly in terms of electronic
effect. During the past few years however, a considerable amount
of data has been accumulated which points out that steric
effect is generally as important as the electronic effect and
in some cases can even become the dominant factor. This fact
has prompted estimations of the steric requirements of bulky
phosphine ligands in terms of cone angle[9]. As R groups in PR_3
become bulkier, the cone angle increases and larger the cone
angle stronger is the basicity of the phosphine (more p
character of lone pair). The importance and utility of the cone
angle concept has been delineated in several recent publica-
tions[10].

Turning to equilibrium (1), the cone angles are expected
to increase in the order triphenylphosphine, tri-p-tolylphosphine,
tri-m-tolylphosphine. The equilibrium constants (Table IV.1,
IV.2 and IV.3) clearly follow the order expected from cone
angle consideration. In the case of tri-o-tolylphosphine, the
correlation between basicity and cone angle is not that useful
since the coordinating ability of the phosphine is very much
reduced due to excessive congestion around the bonding face of
the P atom.

Equilibrium (1) has a parallel[11] in the reaction (6):

$$(h^5\text{-}C_5H_5)Mo(CO)_3CH_3 + L \rightleftharpoons (h^5\text{-}C_5H_5)Mo(CO)_2L\ COCH_3 \quad \ldots\ldots(6)$$
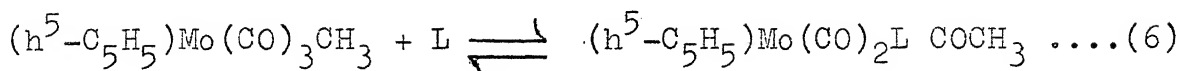
Here the equilibrium constants follow the increasing order triphenylphosphine, tri-p-tolylphosphine. Tri-o-tolylphosphine does not react at all (like equilibrium(1)). Unfortunately the reaction with tri-m-tolylphosphine was not reported by these authors.

c. Reaction with 1,2-bis(diphenylphosphino)ethane

When $Pd_2(Meaao)_2X_2$ is allowed to react with two equivalents of the bidentate phosphine 1,2-bis(diphenylphosphino)ethane (abbreviated hereafter as diphos) in benzene, VI separates out as orange crystalline solid

$$Pd_2(Meaao)_2X_2 + 2\ Ph_2PCH_2CH_2PPh_2 \longrightarrow 2 \left[\begin{array}{c} \text{structure VI} \end{array} \right] \ldots(7)$$
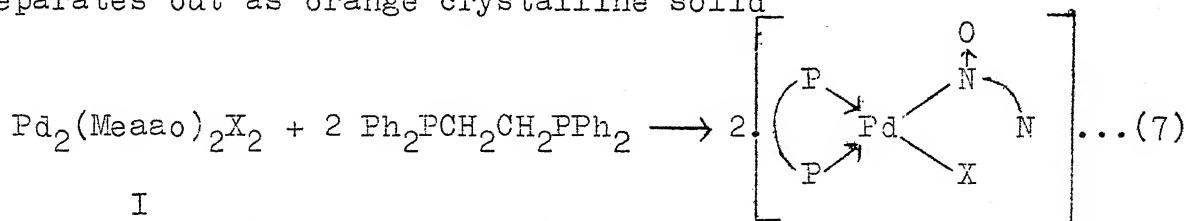
$$\text{I}$$

(R = Me, X= Cl, Br)   VI

In case with X = Br, small amount of (diphos)$PdBr_2$ is deposited in the initial stage of the reaction which is filtered off; orange needles of VI deposit on concentrating the filtrate.

The complexes VI dissolve in chloroform and dichloromethane to give yellow solutions. The electronic spectra exhibit no asborption in the 500 nm region. Clearly the aao chelate ring

in VI is completely open. Unlike III, where in solution a
fraction of the open-ring species is converted to the closed-
ring species II by phosphine dissociation followed by ring-
closure, VI always exists in the open-ring configuration since
the stable diphos chelate ring does not allow the aao fragment
to complete chelation. The electronic spectrum of
$\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{Cl}\right]$ in chloroform is displayed in Fig. IV.5.

The region 1600-1000 cm^{-1} in the infrared spectra of
VI is quite similar to that observed with III. Absorption
around 1490 cm^{-1} is clearly suggestive of the open-azo configu-
ration of the aao fragment. Since in VI Cl is _trans_- to
phosphorus which is a strong _trans_-labilising center, $\nu_{\text{Pd-Cl}}$
appears at a lower energy (312 cm^{-1}) compared to that of
III (335 cm^{-1}) where Cl is _trans_- to the oximato group of the
aao fragment. The major infrared vibrations of VI are set out
in Table IV.4 and one representative spectrum is shown in
Fig. IV.6.

The pmr spectra of $\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{X}\right]$ complexes
exhibit a high-field shift for the methyl group of the aao
fragment (Table IV.5). Similar high-field shifts (of greater
magnitude) are also observed for the complexes III due to
anisotropic diamagnetic shielding by the phenyl groups of the
phosphine (section IV.2.A.a). The lesser magnitude of high-
field shift in case of $\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{X}\right]$ can be attributed
to the fact that in these complexes the methyl group of the

FIG Ⅳ.5. ELECTRONIC SPECTRUM OF [(Meaao)Pd(diphos)Cl] IN CHLOROFORM.

INFRARED DATA OF $[(Meaao)Pd(diphos)X]$ AND $[(Meaao)Pd(arphos)X]$ COMPLEXES IN KBr DISCS (FREQUENCIES ARE IN cm^{-1})[a]

Compound	ν_{C-H} R	ν_{C-H} Ar	ν_{N-O}	ν_{Pd-Cl}	Other Vibrations
[(Meaao)Pd(diphos)Cl]	2960(w), 2920(w)	3060(m)	1250(vs)	312(m)	1490(m),1480(s),1430(s),1340(s), 1100(s),1000(m),880(m),820(m),760(m), 740(s),700(s),680(vs),590(m),555(m), 530(s),480(m).
[(Meaao)Pd(arphos)Cl]	2920(w)	3040(m)	1255(vs)	312(m)	1490(m),1480(s),1430(s),1340(s), 1100(s),1000(m),860(m),800(m),760(m), 740(s),705(m),680(vs),590(m),555(m), 520(s),480(s).
[(Meaao)Pd(diphos)Br]	2940(w), 2900(w)	3040(m)	1250(vs)	—	1490(m),1480(s),1430(s),1340(s), 1100(s),990(m),870(m),815(m),760(m), 740(m),700(s),680(vs),585(m),550(m), 525(s),480(m).
[(Meaao)Pd(arphos)Br]	2940(w), 2900(w)	3050(m)	1250(vs)	—	1490(m),1480(s),1430(s),1340(s), 1100(s),1000(m),860(m),805(m),765(m), 740(s),710(m),680(vs),590(m),550(m), 520(s),480(s).
[(Meaao)Pd(PPh$_3$)$_2$Cl]	2920(w)	3040(m)	1265(vs)	335(m)	1490(m),1480(s),1430(s),1345(m), 1095(s),1000(m),760(m),740(s),690(s), 590(m),515(s),500(m),490(m).

a. The compound $[(Meaao)Pd(PPh_3)_2Cl]$ has been included in this table for the sake of comparison
w = weak; m = medium; s = strong; and vs = very strong.

FIG IV.6. PARTIAL INFRARED SPECTRUM OF $[(\text{Meaao})Pd(\text{diphos})Cl]$ IN KBr (Disc)

TABLE IV.5

^{1}H CHEMICAL SHIFTS^a OF $\left[\text{(Meaao)Pd(diphos)X} \right]$ COMPLEXES

SOLVENT: CDCl$_3$.

Compound	Group	Chemical Shift δ (ppm)
$\left[\text{(Meaao)Pd(diphos)Cl} \right]$	aao CH$_3$	1.80
	bridge CH$_2$ (of phosphine)	2.33,2.53
$\left[\text{(Meaao)Pd(diphos)Br} \right]$	aao CH$_3$	1.80
	bridge CH$_2$ (of phosphine)	2.20,2.40

a Aromatic protons give signals in the region 6.80-8.20 ppm and are not tabulated.

aao fragment lies somewhat away from the phenyl groups of the less flexible (chelated) phosphine and thus possibly is less shielded. Free diphos shows a case of 'virtual coupling' and a triplet at δ = 2.15 ppm is observed for the bridge methylene protons[12]. In [(Meaao)Pd(diphos)X], this situation is no longer there; a normal spectrum (equivalent CH_2 groups) with two CH_2 signals ($^2J_{PH}$ = 20 Hz) is observed for both X = Cl and Br. Studies to understand the reasons for the change in the nature of coupling are in progress. The room temperature pmr spectrum of [(Meaao)Pd(diphos)Cl] in $CDCl_3$ is displayed in Fig. IV.7.

d. Reaction with 1-diphenylphosphino-2-diphenylarsinoethane

The 2:1 reaction (in benzene) of the bidentate ligand 1-diphenylphosphino-2-diphenylarsinoethane(abbreviated hereafter as arphos) with $Pd_2(Meaao)_2X_2$ yields open-azo species [(Meaao)Pd(arphos)X] exactly analogous to VI. The orange crystalline products dissolve in chloroform or dichloromethane (moderately soluble) to give yellow solution . No absorption around 500 nm is recorded in these solutions. Thus even in solution, the aao fragment in [(Meaao)Pd(arphos)X] remains completely open. It is interesting to note that though tri-phenylarsine cannot open the aao chelate ring (Chapter III and Section IV.2.A.b), arphos can do the same due to chelate effect. The ring stability of the arphos chelate ring renders the As-end able to compete with the aao fragment for the coordination site

AROMATIC
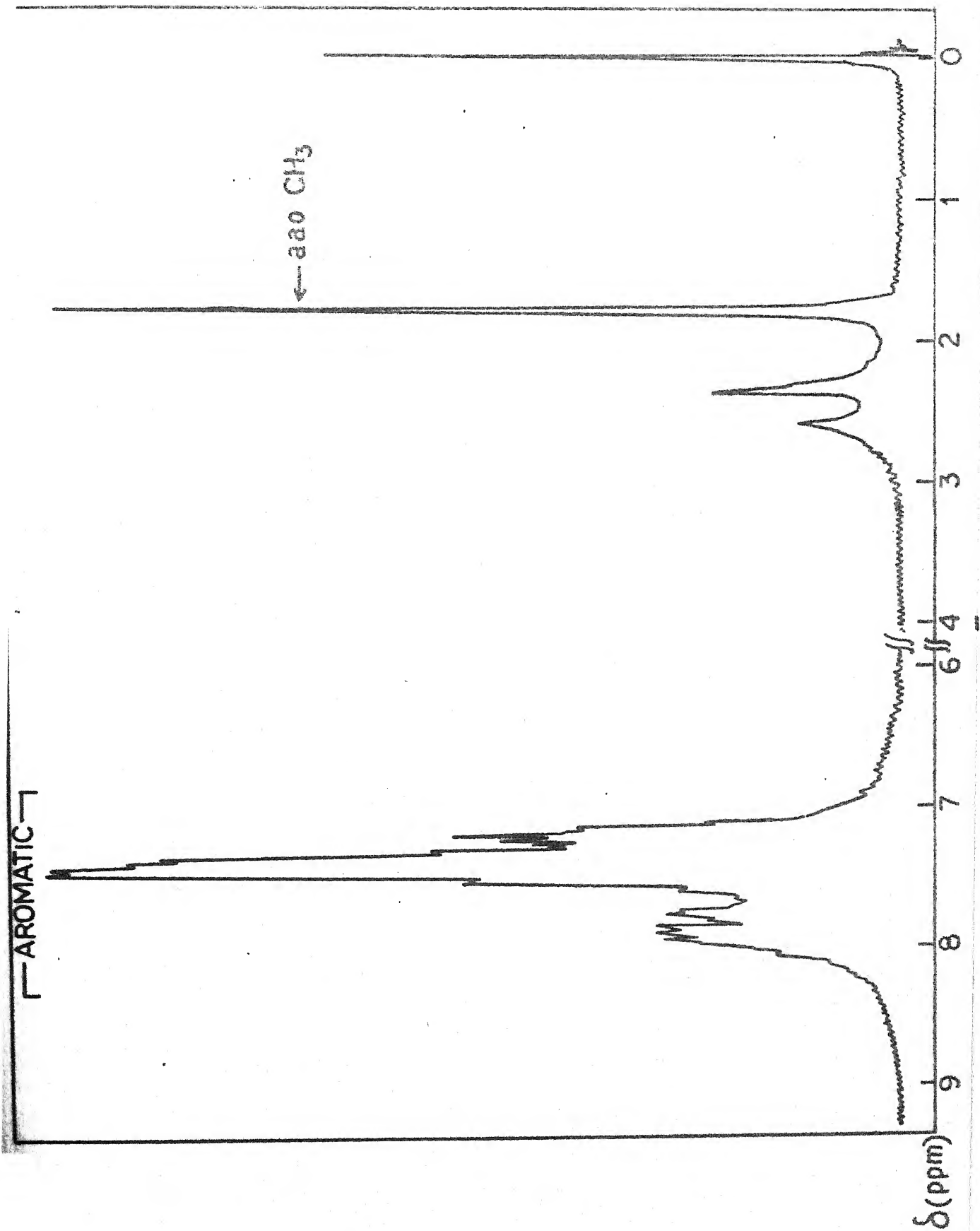
←—a2o CH₃

δ(ppm)

The stereochemistry of $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{X}\right]$ is a bit ambiguous since X can occupy the position _trans_- to either the P center (VIIa) or the As center (VIIb). $\nu_{\text{Pd-Cl}}$ in
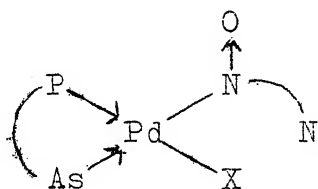
| VIIa | VIIb |
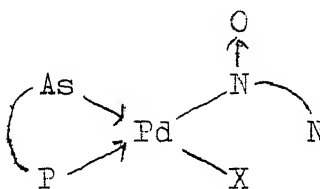
$\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{Cl}\right]$ appears at exactly the same position (312 cm^{-1}) as that in $\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{Cl}\right]$. The Pd-Cl stretching frequencies in _cis_-$\left[(\text{EMe})_3\text{PdCl}_2\right]$ change considerably when E is changed from P to As[4,13]. The appearance of $\nu_{\text{Pd-Cl}}$ in $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{Cl}\right]$ in the same position as that in $\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{Cl}\right]$ suggests that in $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{X}\right]$, X possibly occupies the position _trans_- to the P center (i.e. structure VIIa). The infrared spectra of $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{X}\right]$ complexes are more or less identical to those of the corresponding diphos complexes and the major infrared vibrations are set out in Table IV.4. The pmr spectra of $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{X}\right]$ complexes could not be run because of low solubility in CDCl$_3$.

e. Reaction of the open-azo species $\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{X}\right]$ and $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{X}\right]$ with Pd$_2$(Meaao)$_2$X$_2$

The open-azo species $\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{X}\right]$ VI and $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{X}\right]$ VIIa undergo an extremely facile reaction(8)

with $Pd_2(Meaao)_2X_2$ in benzene or dichloromethane. When two equivalents of VI (or VIIa) are added to one equivalent of $Pd_2(Meaao)_2X_2$ in benzene (or dichloromethane), the initial violet color changes to deep green due to formation of the bis-arylazo-oximate VIII and $(diphos)PdX_2$ (or $(arphos)PdX_2$) separates out as grey crystalline solid. Both the products of reactions (8) have

$$Pd_2(Meaao)_2X_2 + 2\ \text{[I]} \longrightarrow 2\ \text{[VIII]} + 2\ \text{[IX]} \quad ..(8)$$

| I | VI or VIIa | VIII | IX |

$(R=Me,\ X=Cl,Br)$

been isolated and characterised.

The probable rationalisation of reaction (8) is represented in Scheme 1. The intermediacy of X (where the aao fragment bridges between two palladium atoms) however, is not confirmed so far.

Another interesting reaction which also leads to the same products namely VIII and IX is the 1:1 reaction (in benzene or dichloromethane) between $Pd_2(Meaao)_2X_2$ and diphos or arphos.

$$Pd_2(Meaao)_2X_2 + diphos(arphos) = \text{[VIII]} + \text{[IX]} \quad ...(9)$$

| I | VIII | IX |

$(R = Me,\ X = Cl,Br)$

FIG IV. 5. ELECTRONIC SPECTRUM OF $[(Meaao)Pd(diphos)Cl]$ IN CHLOROFORM.

INFRARED DATA OF $[(Meaao)Pd(diphos)X]$ AND $[(Meaao)Pd(arphos)X]$ COMPLEXES IN KBr DISCS (FREQUENCIES ARE IN cm^{-1})[a].

Compound	ν_{C-H}		ν_{N-O}	ν_{Pd-Cl}	Other Vibrations
	R	Ar			
$[(Meaao)Pd(diphos)Cl]$	2960(w), 2920(w)	3060(m)	1250(vs)	312(m)	1490(m),1480(s),1430(s),1340(s), 1100(s),1000(m),880(m),820(m),760(m), 740(s),700(s),680(vs),590(m),555(m), 530(s),480(m).
$[(Meaao)Pd(arphos)Cl]$	2920(w)	3040(m)	1255(vs)	312(m)	1490(m),1480(s),1430(s),1340(s), 1100(s),1000(m),860(m),800(m),760(m), 740(s),705(m),680(vs),590(m),555(m), 520(s),480(s).
$[(Meaao)Pd(diphos)Br]$	2940(w), 2900(w)	3040(m)	1250(vs)	—	1490(m),1480(s),1430(s),1340(s), 1100(s),990(m),870(m),815(m),760(m), 740(m),700(s),680(vs),585(m),550(m), 525(s),480(m).
$[(Meaao)Pd(arphos)Br]$	2940(w), 2900(w)	3050(m)	1250(vs)	—	1490(m),1480(s),1430(s),1340(s), 1100(s),1000(m),860(m),805(m),765(m), 740(s),710(m),680(vs),590(m),550(m), 520(s),480(s).
$[(Meaao)Pd(PPh_3)_2Cl]$	2920(w)	3040(m)	1265(vs)	335(m)	1490(m),1480(s),1430(s),1345(m), 1095(s),1000(m),760(m),740(s),690(s), 590(m),515(s),500(m),490(m).

a. The compound $[(Meaao)Pd(PPh_3)_2Cl]$ has been included in this table for the sake of comparison w = weak; m = medium; s = strong; and vs = very strong.

FIG Ⅳ.6. PARTIAL INFRARED SPECTRUM OF [(Meaao)Pd(diphos)Cl] IN KBr (Disc)

TABLE IV.5

^{1}H CHEMICAL SHIFTS^a OF $\left[(\text{Meaao})\text{Pd}(\text{diphos})X \right]$ COMPLEXES

SOLVENT: CDCl$_3$.

Compound	Group	Chemical Shift δ (ppm)
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	bridge CH$_2$ (of phosphine)	2.33, 2.53
$\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{Br} \right]$	aao CH$_3$	1.80
	bridge CH$_2$ (of phosphine)	2.20, 2.40

a Aromatic protons give signals in the region 6.80-8.20 ppm and are not tabulated.

aao fragment lies somewhat away from the phenyl groups of the less flexible (chelated) phosphine and thus possibly is less shielded. Free diphos shows a case of 'virtual coupling' and a triplet at δ = 2.15 ppm is observed for the bridge methylene protons[12]. In $\left[(Meaao)Pd(diphos)X \right]$, this situation is no longer there; a normal spectrum (equivalent CH_2 groups) with two CH_2 signals ($^2J_{PH}$ = 20 Hz) is observed for both X = Cl and Br. Studies to understand the reasons for the change in the nature of coupling are in progress. The room temperature pmr spectrum of $\left[(Meaao)Pd(diphos)Cl \right]$ in $CDCl_3$ is displayed in Fig. IV.7.

d. Reaction with 1-diphenylphosphino-2-diphenylarsinoethane

The 2:1 reaction (in benzene) of the bidentate ligand 1-diphenylphosphino-2-diphenylarsinoethane (abbreviated hereafter as arphos) with $Pd_2(Meaao)_2X_2$ yields open-azo species $\left[(Meaao)Pd(arphos)X \right]$ exactly analogous to VI. The orange crystalline products dissolve in chloroform or dichloromethane (moderately soluble) to give yellow solution . No absorption around 500 nm is recorded in these solutions. Thus even in solution, the aao fragment in $\left[(Meaao)Pd(arphos)X \right]$ remains completely open. It is interesting to note that though triphenylarsine cannot open the aao chelate ring (Chapter III and Section IV.2.A.b), arphos can do the same due to chelate effect. The ring stability of the arphos chelate ring renders the As-end able to compete with the aao fragment for the coordination site.

FIG IV.7. PMR SPECTRUM OF [(Meaao)Pd(diphos)Cl] IN CDCl₄.

The stereochemistry of $\left[(Meaao)Pd(arphos)X\right]$ is a bit ambiguous since X can occupy the position trans- to either the P center (VIIa) or the As center (VIIb). ν_{Pd-Cl} in

VIIa   VIIb

$\left[(Meaao)Pd(arphos)Cl\right]$ appears at exactly the same position (312 cm^{-1}) as that in $\left[(Meaao)Pd(diphos)Cl\right]$. The Pd-Cl stretching frequencies in cis-$\left[(EMe)_3PdCl_2\right]$ change considerably when E is changed from P to As[4,13]. The appearance of ν_{Pd-Cl} in $\left[(Meaao)Pd(arphos)Cl\right]$ in the same position as that in $\left[(Meaao)Pd(diphos)Cl\right]$ suggests that in $\left[(Meaao)Pd(arphos)X\right]$, X possibly occupies the position trans- to the P center (i.e. structure VIIa). The infrared spectra of $\left[(Meaao)Pd(arphos)X\right]$ complexes are more or less identical to those of the corresponding diphos complexes and the major infrared vibrations are set out in Table IV.4. The pmr spectra of $\left[(Meaao)Pd(arphos)X\right]$ complexes could not be run because of low solubility in CDCl$_3$.

e. Reaction of the open-azo species $\left[(Meaao)Pd(diphos)X\right]$ and $\left[(Meaao)Pd(arphos)X\right]$ with Pd$_2$(Meaao)$_2$X$_2$

The open-azo species $\left[(Meaao)Pd(diphos)X\right]$ VI and $\left[(Meaao)Pd(arphos)X\right]$ VIIa undergo an extremely facile reaction(8)

with $Pd_2(Meaao)_2X_2$ in benzene or dichloromethane. When two equivalents of VI (or VIIa) are added to one equivalent of $Pd_2(Meaao)_2X_2$ in benzene (or dichloromethane), the initial violet color changes to deep green due to formation of the bis-arylazo-oximate VIII and (diphos)PdX_2 (or (arphos)PdX_2) separates out as grey crystalline solid. Both the products of reactions (8) have
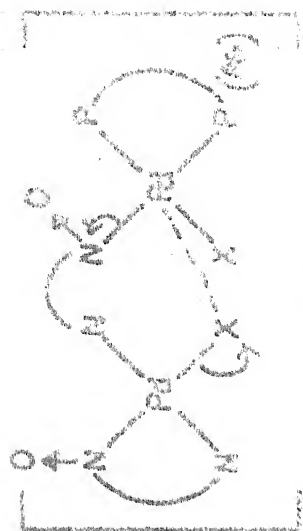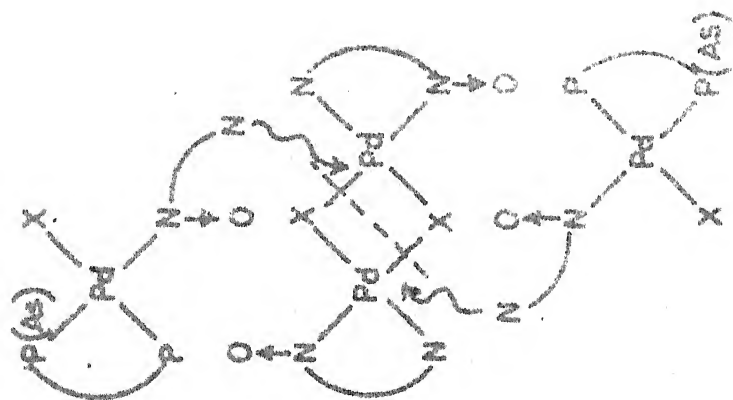
$$Pd_2(Meaao)_2X_2 + 2 \left(\begin{array}{c} P \\ \nearrow Pd \\ P(As) \end{array} \right. \left. \begin{array}{c} \cdots N \\ \searrow X \end{array} \right) \longrightarrow 2 \left(\begin{array}{c} N \\ Pd \\ N \end{array} \right) + 2 \left(\begin{array}{c} P \\ \nearrow Pd \\ P(As) \end{array} \right. \left. \begin{array}{c} X \\ \searrow X \end{array} \right) \quad \ldots (8)$$

<div align="center">

I   VI or VIIa   VIII   IX

</div>

$(R=Me, X=Cl,Br)$

been isolated and characterised.

The probable rationalisation of reaction (8) is represented in Scheme 1. The intermediacy of X (where the aao fragment bridges between two palladium atoms) however, is not confirmed so far.

Another interesting reaction which also leads to the same products namely VIII and IX is the 1:1 reaction (in benzene or dichloromethane) between $Pd_2(Meaao)_2X_2$ and diphos or arphos.

$$Pd_2(Meaao)_2X_2 + diphos(arphos) = \left(\begin{array}{c} N \\ Pd \\ N \end{array} \right) + \left(\begin{array}{c} P(As) \\ \nearrow Pd \\ P \end{array} \right. \left. \begin{array}{c} X \\ \searrow X \end{array} \right) \quad \ldots (9)$$

<div align="center">

I   VIII   IX

</div>

$(R = Me, X = Cl,Br)$

The characteristic green color of VIII develops immediately on mixing one equivalent of diphos or arphos with the violet solution of I (in benzene or dichloromethane) and IX separates out.

Reaction (8) provides a clue for the probable mechanism of reaction (9). First, 0.5 mol of I is converted to one mol of VI (or VIIa) by the one equivalent of diphos (or arphos) added and thus in solution a 1:2 ratio of I and VI (or VIIa) is achieved. The next step is then nothing but reaction (8) which produce VIII and IX (one mol each) as the final products of reaction (9). Dehand[3] has reported the synthesis of a new type of complexes XI in which A-A represents diphos and 1,2-bis(diphenylarsino)ethane and C-N = acetophenone hydrazone
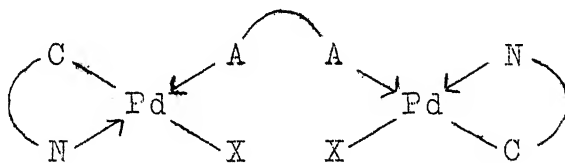
XI

by the 1:1 reaction (in dichloromethane) between the halo-bridged dimer and A-A. The 1:1 reaction (in benzene or dichloromethane) between I and diphos or arphos however, leads to entirely different products.

The reactions of $Pd_2(Meaao)_2X_2$ with diphos and arphos are summerised in Scheme 2.
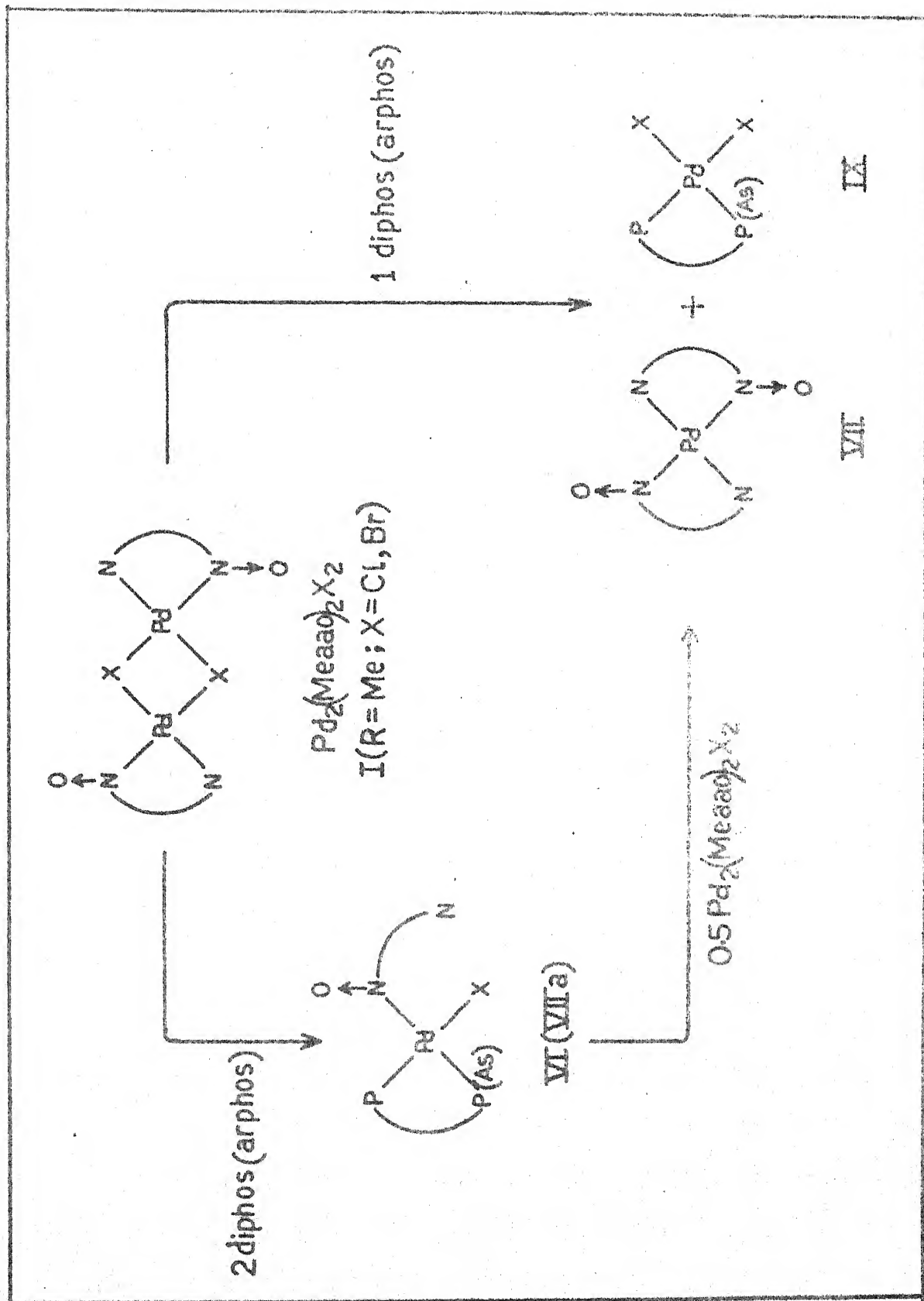
Scheme 2

B. <u>Reaction with HCl: Ring Opening at Oxime-end</u>

a. <u>Reaction of HCl with $Pd_2(Raao)_2Cl_2$ Complexes</u>

The aao chelate ring can be opened at the oxime-end by
the reaction with HCl gas (the same effect is produced by a drop
of concentrated A.R. hydrochloric acid but the reaction with
gas produces a cleaner material).

On introduction of HCl gas into solution of $Pd_2(Meaao)_2Cl_2$
(or $Pd_2(Phaao)_2Cl_2$) in benzene or dichloromethane, the violet
solution (color characteristic of chelated aao fragment) turns
orange-red from which red crystals of XII separates out on
addition of hexane.

$$Pd_2(Raao)_2Cl_2 \xrightarrow[\text{pass HCl gas}]{\text{bz or } CH_2Cl_2} \qquad \cdots(10)$$

I XII

R = Me,Ph
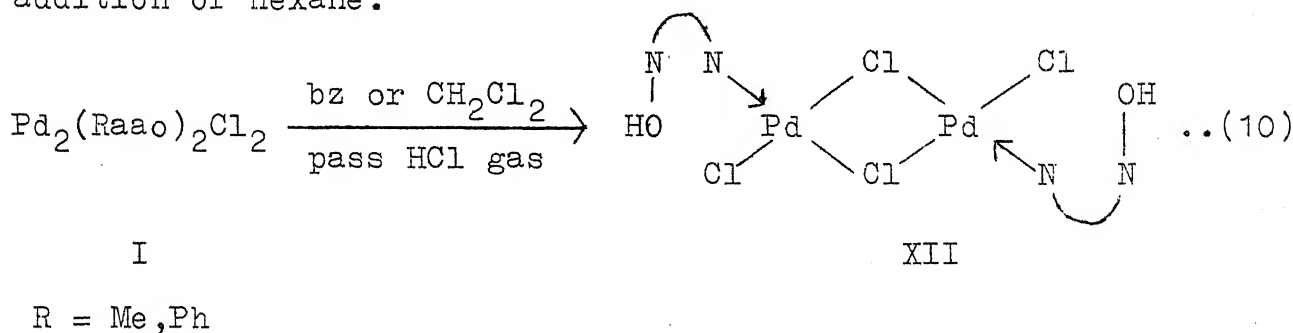
XII is stable only under the solvent saturated with HCl
gas and it is very difficult to isolate it pure in the dry state.
The red crystals of XII start evolving HCl and turning purple
(showing formation of I) soon after the solvent is filtered off.
The conversion XII $\longrightarrow$ I becomes even more facile in presence of
mild bases including water (moist air). Since XII could not be
obtained in pure and dry condition, its structure which is based
on the evidences noted below is to be considered as tentative.

When the orange-red solution which is produced by passing HCl gas into the benzene (or dichloromethane) solution of I is poured into water, I is regenerated in nearly quantitative yield. Further, crystals of XII are rapidly converted to I in contact with water. These observations point out that no other product except XII is formed in reaction (10). It was checked that free HRaao does not undergo any reaction with HCl gas.

Limited examples of opening of chelate ring by reaction with HCl include the glycine[14], acetylacetone[15] and ethylenediamine[16] complexes of palladium (and platinum). In most of the cases, the reaction leads to the displacement of the entire chelate ring yielding $\left[PdCl_4\right]^{2-}$ as the final product.

b. Physical Data for XII

The infrared spectra of XII (R = Me, Ph) were run in KBr discs (the crystals were isolated by quick filtration and immediately made into disc). The KBr discs were red and they remained so during the spectral run (the discs turn purple after 1-2 hrs). The infrared spectrum of XII with R = Me is shown in Fig. IV.8.

Two major infrared vibrations namely ν_{O-H} and $\nu_{Pd-Cl(terminal)}$ provide important clue for the structure of XII. In XII, ν_{O-H} appears as a strong and broad absorption in a relatively low energy region viz $\sim$ 3100 cm^{-1} (Table IV.6).
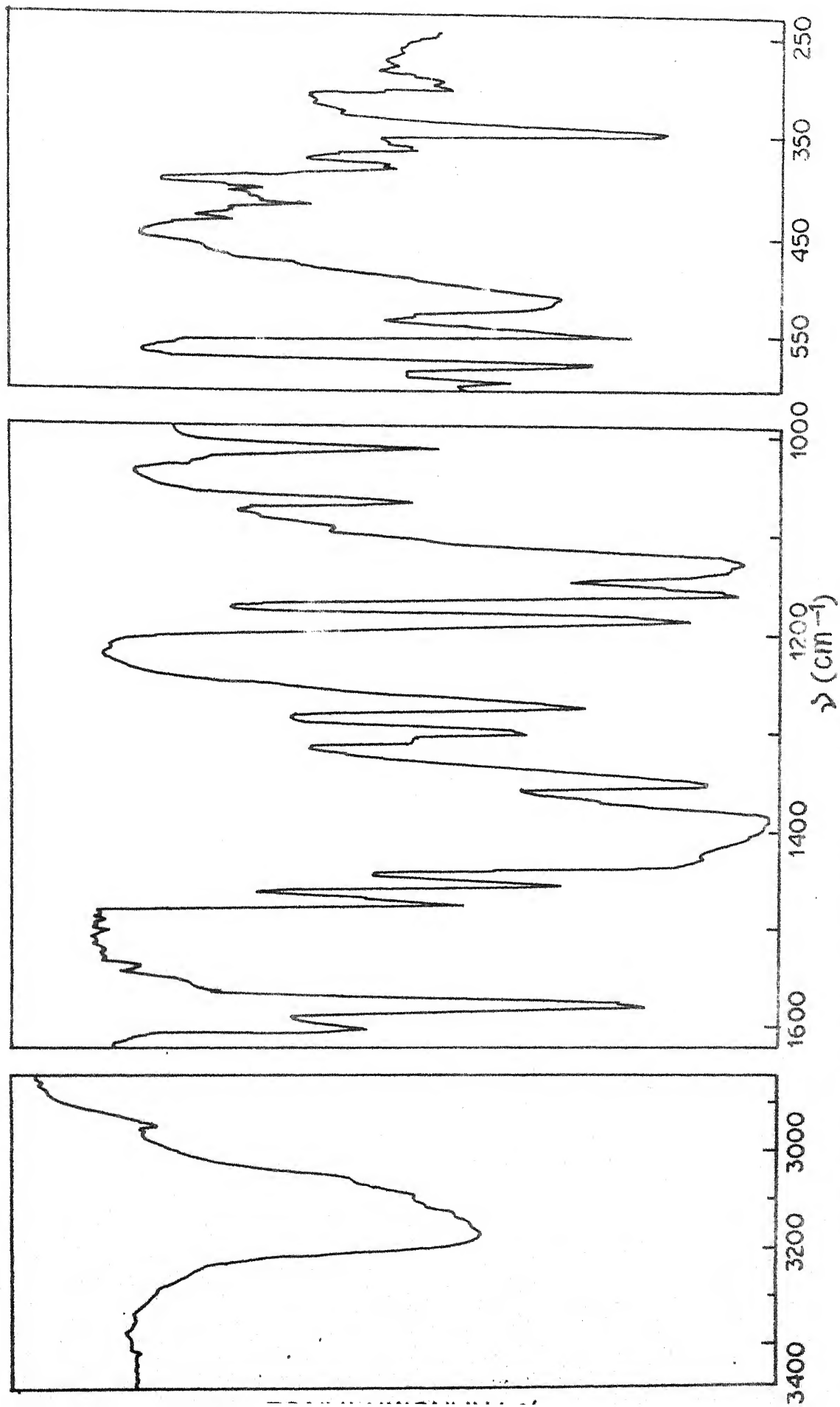
FIG. IV.8. PARTIAL INFRARED SPECTRUM OF $Pd_2(HMeaao)_2Cl_4$ IN KBr (DISC).

(FREQUENCIES ARE IN cm^{-1})

Compound	ν_{O-H}	ν_{Pd-Cl}(terminal)	Other Vibrations
$Pd_2(HMeaao)_2Cl_4$	3140 (s,br)	350 (s)	1575(s),1475(m),1455(m),1430(vs),1390(vs),1355(vs),1310(m),1280(m),1195(s),1170(vs),1135(vs),1075(m),1025(m),1000(m),770(s),710(s),680(s),620(s),610(m),575(m),550(s),515(s),390(m),300(w).
$Pd_2(HPhaao)_2Cl_4$	3100 (m,br)	355 (s)	1590(s),1475(w),1460(m),1405(vs),1320(m),1265(s),1185(s),1165(s),1145(vs),1090(m),1030(m),770(s),720(s),680(s),655(m),605(m),555(m),325(w).

w = weak; m = medium; s = strong; vs = very strong; br = broad.

The low value of ν_{O-H} is most possibly due to intramolecular hydrogen-bonding. $\nu_{Pd-Cl(terminal)}$ at ~ 350 cm^{-1} (Table IV.6) has been identified by comparing the infrared spectra of XII (R = Me, Ph; X = Cl) with the corresponding bromo-species (Chapter II).

The opening of the aao chelate ring at the oxime-end is expected to bring about some change in the position of ν_{N-O}. Comparison of the infrared spectra of XII with the corresponding $Pd_2(Raao)_2Cl_2$ complexes points out to a very strong asborption at ~ 1135 cm^{-1} (Fig. IV.8) which could be ν_{N-O} in XII. Since the region 1400-900 cm^{-1} in the infrared spectra of XII is very complex, no further speculation will be made in this context.

The electronic spectrum of XII (R = Me) in benzene exhibits no absorption around 500 nm. This observation confirms that in XII the aao fragments do not exist in the chelated form. In benzene saturated with HCl gas, XII (R=Me) has one intense band at 385 nm ($\epsilon = 19,500$) which may arise from transition on the coordinated azo group.

The pmr spectra of XII could not be run because they are not sufficiently soluble in CDCl$_3$.

c. Reaction of XII

One reaction viz. the conversion of XII to I in contact with water is already described above. Here the reaction with triphenylphosphine is reported.

Triphenylphosphine is known to open the azo-end of the aao chelate ring (section IV.2.A.a) but not the oxime-end even when used in excess. On addition of excess triphenylphosphine to the benzene solution of XII, yellow crystals of <u>trans-</u> $\left[(PPh_3)_2PdCl_2\right]$ separate out. Displacement of the aao fragment (bound to Pd through the azo-end) from XII with concomitant bridge-splitting by triphenylphosphine is expected to give rise to <u>trans-</u> $\left[(PPh_3)_2PdCl_2\right]$. Thus the isolation of trans-$\left[(PPh_3)_2PdCl_2\right]$ points to the fact that in XII, the oxime-end of the aao fragment is open.

d. <u>Reaction of HCl with the open-azo species $\left[(Meaao)Pd(PPh_3)_2Cl\right]$</u>

The opening of the oxime-end of aao fragment by HCl gas is clearly demonstrated in the reaction (11). When HCl gas is passed through the benzene solution of $\left[(Meaao)Pd(PPh_3)_2Cl\right]$, the initial orange color turns yellow and slowly yellow crystals of <u>trans-</u> $\left[(PPh_3)_2PdCl_2\right]$ are deposited. HMeaao remains in the solution phase.

$$\xrightarrow[\text{pass HCl gas}]{\text{bz}} \quad \text{trans-}\left[(PPh_3)_2PdCl_2\right] + \text{HMeaao}$$

.....(11)

III
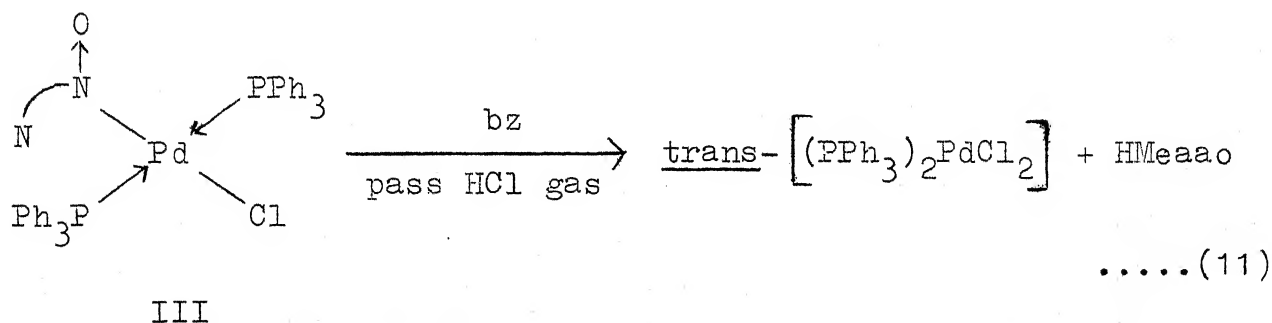
(R = Me, X = Cl)

C. Concluding Remarks

Some of the reactions discussed in the preceeding sections are collectively represented in Scheme 3 taking $Pd_2(Meaao)_2Cl_2$ as the starting compound for the various reactions. Scheme 3 demonstrate that the arylazooximato chelate ring can be opened at either end depending on the attacking reagent. When both reagents (PPh_3 and HCl) are used successively in any order, the entire ligand in eliminated with the formation of trans-$\left[(PPh_3)_2PdCl_2\right]$.

IV.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Chemicals

1,2-bis(diphenylphosphino)ethane(diphos) and 1-diphenylphosphino-2-diphenylarsinoethane(arphos) were procured from Strem Chemicals Inc. (U.S.A.) and were recrystallised from benzene before use. Triarylphosphines (Eastman Organic Chemicals, (U.S.A.)) were recrystallised from dehydrated ethanol.

HCl gas was generated by dropwise addition of concentrated sulphuric acid (A.R Grade) over ammonium chloride (ANALR Grade, Sarabhai Merck Chemicals Pvt. Ltd.(India)).

Scheme 3

b. The Complexes

(i) Synthesis of $[(Meaao)Pd(PPh_3)_2X]$ Complexes

The synthesis of $[(Meaao)Pd(PPh_3)_2Cl]$ is described below.

A mixture of 365 mg (0.6 mmol) of di-μ-chlorobis[phenyl-azoacetaldoximatopalladium(II)] and 629 mg (2.4 mmol) of triphenylphosphine was dissolved in 20 ml of benzene to get a clear orange-red solution. The solution was then allowed to evaporate slowly in vacuum. When the volume of the solution was $\sim$2 ml, orange crystals started depositing. The crystals were collected by filtration, washed with minimum volume of benzene (the complex is highly soluble in organic solvents) and dried in vacuum (yield $\sim$ 60%).

$[(Meaao)Pd(PPh_3)_2Br]$ was prepared by a similar procedure starting from the bromo-bridged arylazooximate $Pd_2(Meaao)_2Br_2$ and triphenylphosphine.

(ii) Synthesis of $[(Meaao)Pd(diphos)X]$ Complexes

The complex $[(Meaao)Pd(diphos)Cl]$ was prepared as follows:

122 mg (0.2 mmol) of di-μ-chlorobis[phenylazoacetald-oximatopalladium(II)] was dissolved in 30 ml of benzene (mild warming) and to this clear violet solution was added with stirring a solution of 160 mg (0.4 mmol) of diphos in 5 ml of

benzene. The color of the solution turned orange and orange
solid started crystallising out. After 15 minutes of stirring
the orange crystals were filtered, washed with benzene and
dried in vacuum (yield $\sim$ 80%).

$\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{Br}\right]$ was synthesised similarly from
$\text{Pd}_2(\text{Meaao})_2\text{Br}_2$ and diphos.

(iii) Synthesis of $\left[(\text{Meaao})\text{Pd}(\text{arphos})\overline{X}\right]$ Complexes

$\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{Cl}\right]$ was synthesised as follows:

122 mg (0.2 mmol) of di-μ-chlorobis$\left[\text{phenylazoacetald-}\right.$
oximatopalladium(II)$\left.\right]$ was dissolved in 30 ml of benzene (mild
warming). To the clear violet solution thus resulted was
quickly added with constant stirring a solution of 190 mg
(a little more than 0.4 mmol) of arphos in 5 ml of benzene.
The color of the solution turned orange and as the stirring
continued, orange crystals separated out. The crystals were
collected by filtration, washed with benzene and finally dried
in vacuum (yield $\sim$ 80%).

The synthesis of $\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{Br}\right]$ follows a similar
procedure.

c. Reaction of $\text{Pd}_2(\text{Meaao})_2\text{X}_2$ with $\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{X}\right]$ and
$\left[(\text{Meaao})\text{Pd}(\text{arphos})\text{X}\right]$.

The reaction between $\text{Pd}_2(\text{Meaao})_2\text{Cl}_2$ and
$\left[(\text{Meaao})\text{Pd}(\text{diphos})\text{Cl}\right]$ is described below.

To a solution (orange in color) of 141 mg (0.2 mmol) of $\left[(Meaao)Pd(diphos)Cl\right]$ in 30 ml of benzene was added with stirring a solution (violet in color) of 61 mg (0.1 mmol) of di-μ-chloro-bis$\left[(phenylazoacetaldoximatopalladium(II)\right]$ in 20 ml of benzene. The color of the mixture turned deep green and slowly grey crystalline precipitate of (diphos)$PdCl_2$ came down. After the precipitated (diphos)$PdCl_2$ was filtered off, the green filtrate was concentrated and 5 ml of hexane was added to it when dark crystals of bis(phenylazoacetaldoximato)palladium(II) separated. The crystals were collected by filtration, washed with hexane and dried in air.

d. 1:1 Reaction between $Pd_2(Meaao)_2X_2$ and diphos (or arphos)

The reaction with diphos is described here.

A solution of 80 mg (0.2 mmol) of diphos in 5 ml of benzene was added with stirring to a solution of 122 mg (0.2 mmol) of di-μ-chlorobis$\left[phenylazoacetaldoximatopalladium(II)\right]$ in 25 ml of benzene when the initial violet color turned deep green and (diphos)$PdCl_2$ crystallised out. (diphos)$PdCl_2$ was collected from the green solution by filtration. Dark crystals of bis(phenylazoacetaldoximato)palladium(II) were collected from the green filtrate by concentrating it to small volume and adding hexane.

The observations and results obtained in the other reactions are similar.

e. <u>Generation of the Open-oxime Species</u> $Pd_2(HRaao)_2Cl_4$ (XII)

The procedure for the generation of $Pd_2(HMeaao)_2Cl_4$ is as follows:

A slow stream of HCl gas was passed through a solution of $Pd_2(Meaao)_2Cl_2$ ($\sim$50 mg) in benzene ($\sim$ 20 ml). The initial violet color turned orange-red. Addition of 10 ml of hexane to this orange-red solution precipitated red crystals of $Pd_2(HMeaao)_2Cl_4$.

In order to prepare the KBr disc, $Pd_2(HMeaao)_2Cl_4$ was collected by decanting the mother liquor and quickly transferring the red slurry to KBr power. Remaining trace of benzene evaporated during the preparation of the KBr disc.

Since $Pd_2(Phaao)_2Cl_2$ is sparingly soluble in benzene the open-oxime species $Pd_2(HPhaao)_2Cl_4$ was obtained in the following way.

About 30 mg of $Pd_2(Phaao)_2Cl_2$ was suspended in 20 ml of benzene and through it a stream of HCl gas was passed while the whole mixture was stirred thoroughly. Slowly the purple solid turned red. The passage of HCl was continued until the entire solid (and the mother liquor) was completely red. $Pd_2(HPhaao)_2Cl_4$ thus prepared was collected for infrared measurement in the same way as described above.

f. Reaction of $\left[(\text{Meaao})\text{Pd}(\text{PPh}_3)_2\text{Cl}\right]$ with HCl

A slow stream of HCl gas was introduced into a solution of 100 mg of $\left[(\text{Meaao})\text{Pd}(\text{PPh}_3)_2\text{Cl}\right]$ in 15 ml of benzene. As a few bubbles of HCl were passed through the orange-red solution, the color changed to pale yellow and yellow crystals of trans-$\left[(\text{PPh}_3)_2\text{PdCl}_2\right]$ were deposited. The crystals were collected by filtration, washed thoroughly with ethanol and dried over fused $CaCl_2$. Free phenylazoacetaldoxime was isolated by evaporating the filtrate to dryness and recrystallising the residue from ethanol.

B. Characterisation of Complexes

This was done by C, H, N microanalysis and metal analysis. Characterisation data for the complexes are collected in Table IV.7.

C. Physical Measurements

a. Infrared Spectra

Details are given in Chapter II.

b. Electronic Spectra

Details are given in Chapter II.

c. Proton Magnetic Resonance Spectra

Details are given in Chapter II.

TABLE IV.41

CHARACTERISATION DATA OF PALLADIUM(II) COMPLEXES

Compound	MP^{o}C^{a,b}	% C		% H		% N		% Pd	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
[(Meaao)Pd(diphos)Cl]	199	58.11	58.02	4.59	4.61	5.98	5.83	15.15	15.20
[(Meaao)Pd(diphos)Br]	190	54.65	54.55	4.32	4.31	5.62	5.67	14.20	14.31
[(Meaao)Pd(arphos)Cl]	170	54.67	54.62	4.32	4.30	5.62	5.59	14.25	14.13
[(Meaao)Pd(arphos)Br]	165	51.60	51.24	4.07	4.10	5.31	5.28	13.45	13.40
[(Meaao)Pd(PPh$_3$)$_2$Cl]	105-115	63.75	63.41	4.62	4.51	5.07	5.18	12.84	12.70

a All melting points reported in this table are uncorrected.

b All the complexes melt with decomposition.

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CHAPTER   V

REACTIONS OF BIS-ARYLAZOOXIMATES OF

PALLADIUM(II)

CHAPTER V

REACTIONS OF BIS-ARYLAZOOXIMATES OF
PALLADIUM(II)

Abstract: The ring-opening and oxidative reactions of the
bis-arylazooximates are discussed. Amines (am) like pyridine,
aniline, γ-picoline and ammonia open one arylazooximato (aao)
chelate ring (at azo-end) in $Pd(Raao)_2$ to produce $\left[(Raao)_2Pd(am)\right]$
in solution. These species exhibit an intense band at ~ 500 nm
with $\epsilon \sim 7000$. All attempts to isolate the complexes in solid
state failed. With one equivalent of triphenylphosphine (PPh_3),
$Pd(Meaao)_2$ yields $\left[(Meaao)_2Pd(PPh_3)\right]$ which can be isolated as
a violet crystalline solid. When a solution (in benzene)
containing $Pd(Meaao)_2$ and two equivalents of PPh_3 is evaporated
to a small volume, orange crystals of $\left[(Meaao)_2Pd(PPh_3)_2\right]$
separate out. Infrared spectrum of $\left[(Meaao)_2Pd(PPh_3)_2\right]$ in KBr
indicates that in solid state both the aao fragments exist in
open-azo configuration and the two PPh_3 molecules are _trans_-
to each other. In solution $\left[(Meaao)_2Pd(PPh_3)_2\right]$ spontaneously
dissociate into $\left[(Meaao)_2Pd(PPh_3)\right]$ and PPh_3. In the room tempera-
ture pmr spectrum of $\left[(Meaao)_2Pd(PPh_3)\right]$, one broad methyl signal
is recorded which is a weighted average of the methyl signals
of the fast exchanging chelated and open aao fragment. The
reactions of tri-_m_-tolylphosphine and tri-_p_-tolylphosphine

with Pd(Meaao)$_2$ are similar to that between PPh$_3$ and Pd(Meaao)$_2$.
Both tri-o-tolylphosphine and triphenylarsine are unable to open
the aao chelate rings in Pd(Meaao)$_2$. Stable palladium complexes
with two aao fragments in open-azo configuration have been
synthesised by reacting Pd(Meaao)$_2$ with Ph$_2$PCH$_2$CH$_2$PPh$_2$ (diphos)
and Ph$_2$PCH$_2$CH$_2$AsPh$_2$ (arphos). The complexes $\left[(Meaao)_2Pd(diphos) \right]$
and $\left[(Meaao)_2Pd(arphos) \right]$ exhibit no electronic band around
500 nm both in solid state and in solution. The mixed complex
Pd(Meaao)(azbz) reacts with one mol of PPh$_3$ to yield
$\left[(Meaao)Pd(azbz)(PPh_3) \right]$ in which the aao fragment exists in
open-azo configuration (ir and pmr data).

Passage of HCl gas through solutions of Pd(Raao)$_2$ in
benzene results in the formation of Pd$_2$(HRaao)$_2$Cl$_4$ complexes
with simultaneous rejection of one mol of HRaao per Pd atom.
When mild bases (including water) are added to the reaction
mixture, the bis-complexes are regenerated.

The oxidative addition of two mols of HMeaao to one mol
of $\left[Pd(PPh_3)_4 \right]$ leads to the formation of $\left[(Meaao)_2Pd(PPh_3)_2 \right]$.
Oxidation of Pd(Raao)$_2$ with dichlorine and dibromine in benzene
(or chloroform) produces deep red solutions which are believed
to contain unstable Pd(IV) species. When the red solutions are
heated or allowed to react with ethanol, Pd$_2$(Raao)$_2$X$_2$ complexes
are precipitated. Excess halogens bring about complicated
reactions producing PdX$_2$ and other unidentified organic
compounds.

V.1 INTRODUCTION

Among the various reactions of bis-arylazooximates
of palladium(II) i.e. Pd(Raao)$_2$ (R = Me, Ph, p-tol), reactions
which lead to opening of the aao chelate ring are of interest.
The various interesting results described in Chapter IV provide
an insight to the mechanisms of the ring-opening reactions. Acc-
ordingly syntheses of species containing either or both of
the aao chelate rings open have been attempted. This chapter
concerns the results of such investigations together with the
reactions of the bis-complexes with HCl. Oxidative additions
of arylazooximes and halogens to $\left[Pd(PPh_3)_4\right]$ and Pd(Raao)$_2$
respectively are also described. One particular reaction
namely the 1:1 reaction of Pd(Raao)$_2$ with Pd(PhCN)$_2$X$_2$ or
PdX$_2$ (X = Cl, Br) in ethanol (or benzene) has already been
described in Chapter II Section II.2.A.d.

V.2 RESULTS AND DISCUSSION

A. Reactions of Pd(Raao)$_2$ with Amines

Addition of amines like pyridine, aniline or
$\curlyvee$-picoline to solutions of bis-arylazooximates in benzene
(or chloroform) brings about a sharp color change from green
to red. The red solutions on dilution with benzene (or chloro-
form) turn green showing the regeneration of the bis-complexes.

The electronic spectra of $Pd(Meaao)_2$ in pyridine and aniline exhibit an intense band at 500 nm with extinction coefficient of $\sim$ 7000. It was seen earlier that presence of one closed aao chelate ring per Pd atom gives rise to an allowed transition around 500 nm. Thus the species in solution probably has only one chelated aao fragment with the second aao group bound at the oxime-end (structure I).

$$
\begin{array}{c}
O \\
\uparrow \\
N \\
\end{array}
\quad \xleftarrow{\text{am}}
$$
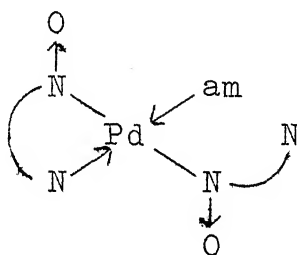
I

Attempts to isolate complexes of the type I from the red solutions however, failed. Even complete evaporation of solutions of bis-complexes in benzene containing stoichiometric amounts of amines yielded gummy products. Bis-complexes with R = aryl dissolve freely in pyridine (purple solutions) but crystallise out unchanged on slow evaporation. The electronic spectra of $Pd(Meaao)_2$ and $Pd(\underline{p}\text{-tolaao})_2$ in pyridine are displayed in Fig.V.1 and the spectral data are collected in Table V.1.

Passage of ammonia gas through solutions of bis-arylazo-oximates in benzene (or chloroform) also produces similar green to red color change. The characteristic green color of the bis-complexes reappears when the red solutions are boiled or
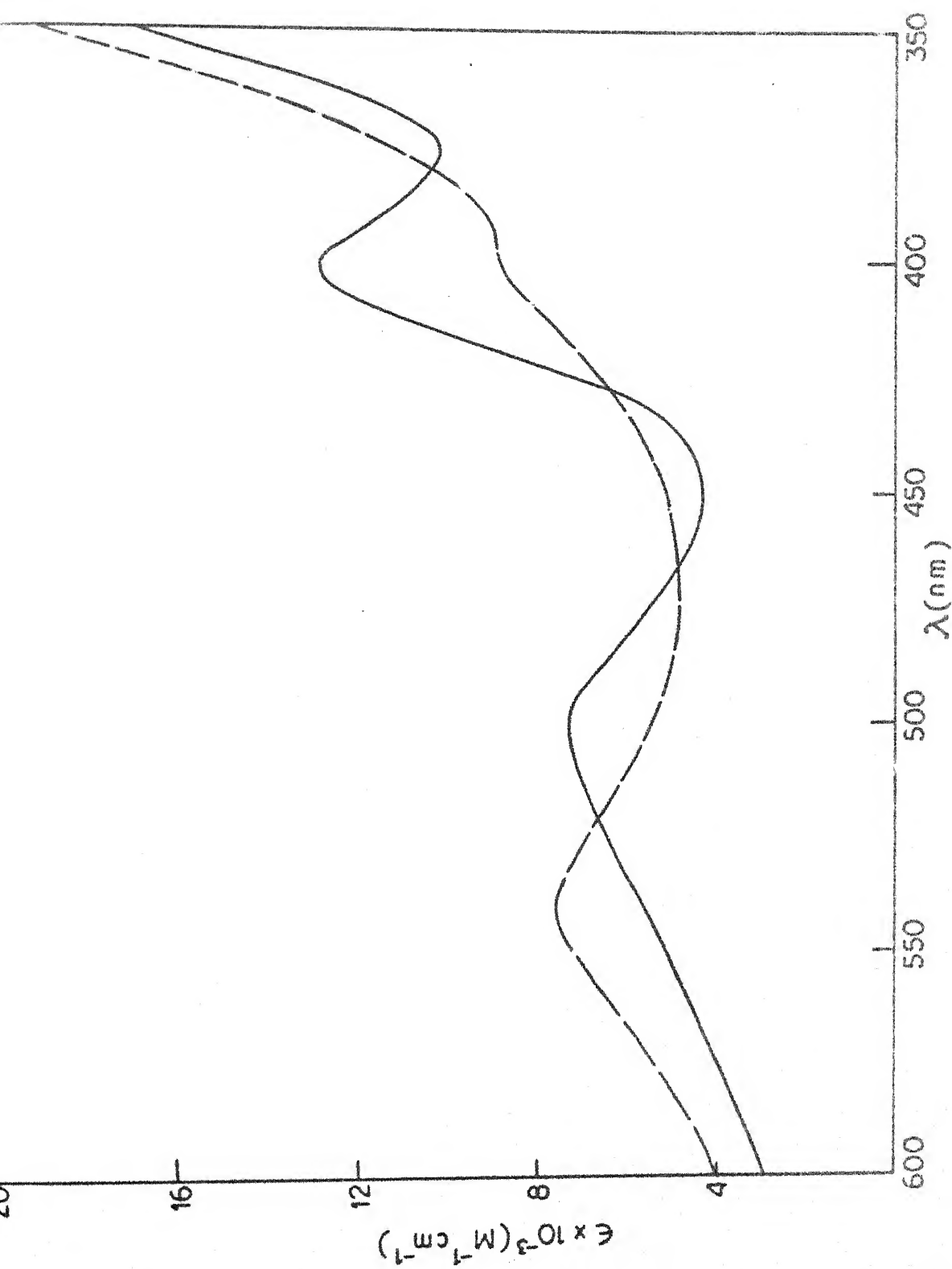
FIG.Ⅴ.1. ELECTRONIC SPECTRA OF Pd (Meaao)$_2$ (———) AND Pd (p-tolaao)$_2$ (———) IN PYRIDINE.

λ(nm)

$\epsilon \times 10^{-3} (M^{-1} cm^{-1})$

POSITIONS (λ nm) AND INTENSITIES (ϵ $M^{-1}cm^{-1}$) OF THE NEAR 500 nm BAND OF $[(Raao)_2Pd(DONOR)]$ COMPLEXES IN DIFFERENT SOLVENTS AND AT ROOM TEMPERATURE

Compound	Solvent	λ (ϵ)
$[(Meaao)_2Pd(py)]$	Pyridine	500 (7000)
$[(Meaao)_2Pd(aniline)]$	Aniline	500 (7400)
$[(p-tolaao)_2Pd(py)]$	Pyridine	540 (7200)
$[(Meaao)_2Pd(PPh_3)]$	Benzene	500 (7000)
$[(Meaao)_2Pd(P(m-tol)_3)]$	Benzene	500 (7000)
$[(Meaao)_2Pd(P(p-tcl)_3)]$	Benzene	500 (7500)

nitrogen gas is passed through them. Thus amines like pyridine, aniline, γ-picoline and ammonia behave in the same manner. In no case the second aao chelate ring was found to be open even in the presence of large excess of amines. Once the red color ($\lambda \sim 500$ nm; $\epsilon \sim 7000$) has fully developed, further addition of amine does not alter the electronic spectrum. If both rings would have opened, the ~ 500 nm band would have progressively disappeared.

B. Reaction with Triphenylphosphine

Having failed to isolate authentic crystalline amine adducts the reaction with triphenylphosphine was investigated with the hope of getting more well-defined systems. The investigation was mostly limited to $Pd(Meaao)_2$ since the complexes $Pd(Raao)_2$ with R = aryl are sparingly soluble in organic solvents.

Addition of one equivalent of PPh_3 to the solution of $Pd(Meaao)_2$ in benzene (green in color) produces a deep red solution. On evaporating the solution to dryness (in vacuum) a violet solid is obtained which on recrystallisation from boiling hexane yields violet crystals of $\left[(Meaao)_2 Pd(PPh_3)\right]$.

The infrared spectrum of $\left[(Meaao)_2 Pd(PPh_3)\right]$ exhibit characteristic absorptions of both open and closed aao chelate rings (Fig. V.2 and Table V.2). In the electronic spectrum
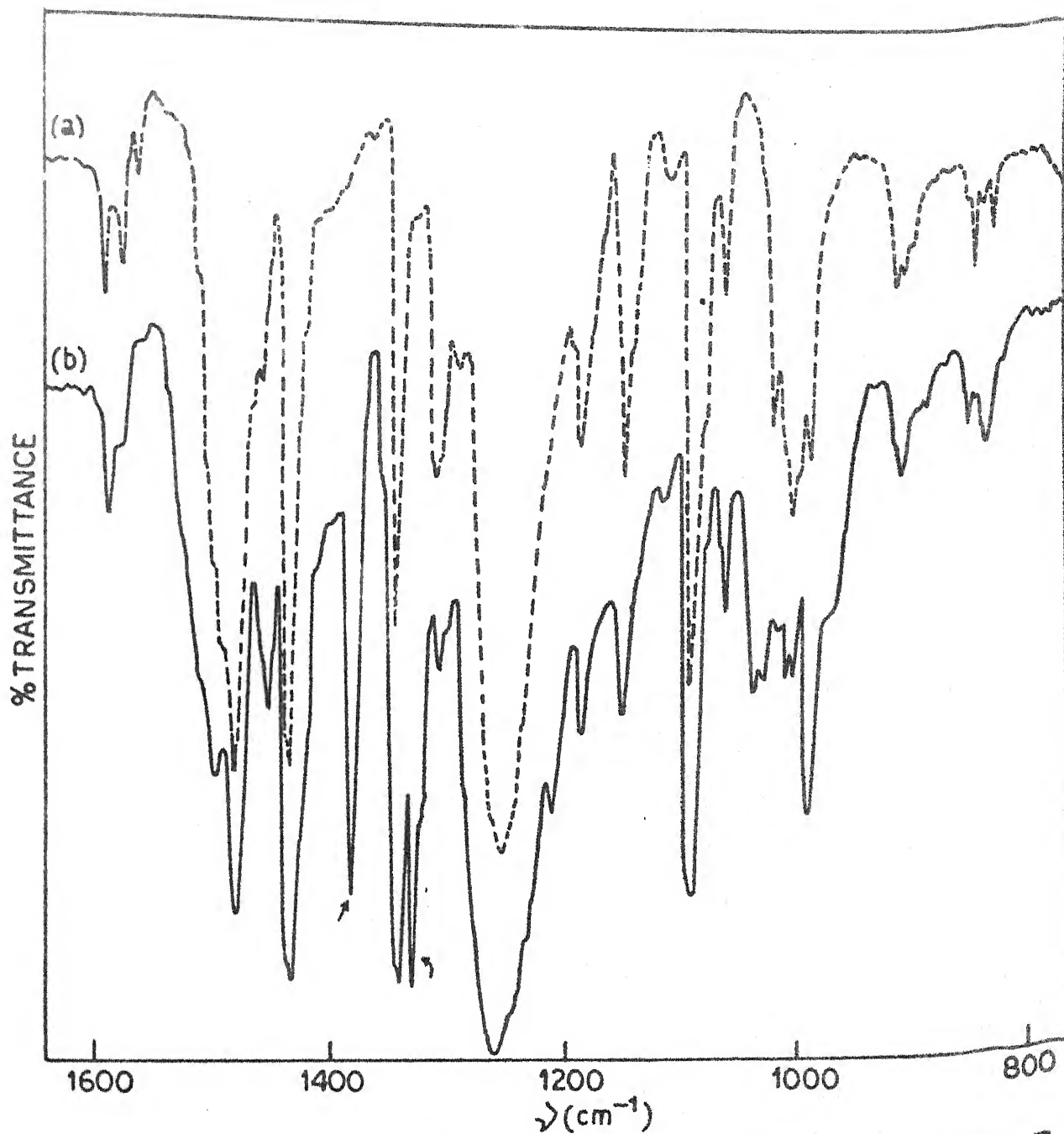
FIG. V. 2. PARTIAL INFRARED SPECTRA OF (a) $[(Meaao)_2 Pd(PPh_3)_2]$ AND (b) $[(Meaao)_2 Pd(PPh_3)]$ IN KBr (DISC). THE MARKED ABSORPTIONS ARE CHARACTERISTIC OF CHELATED aao RING.

of $\left[(\text{Meaao})_2\text{Pd}(\text{PPh}_3)\right]$ in benzene, an intense band at 500 nm ($\epsilon = 7000$) is observed. Therefore, the complex is believed to have the structure II.
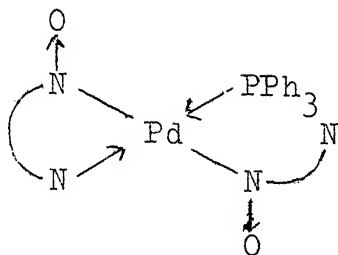
II

The room temperature pmr spectrum of $\left[(\text{Meaao})_2\text{Pd}(\text{PPh}_3)\right]$ in CDCl_3 shows only one broad methyl signal at $\delta = 1.82$ ppm. The broadening of the methyl signal probably arise from fast exchange between open and closed aao ring i.e. the signal is a weighted average of the methyl signals for the chelated aao and the open aao fragment in II. The exchange process can be written as follows:

$$\ldots\ldots(1)$$
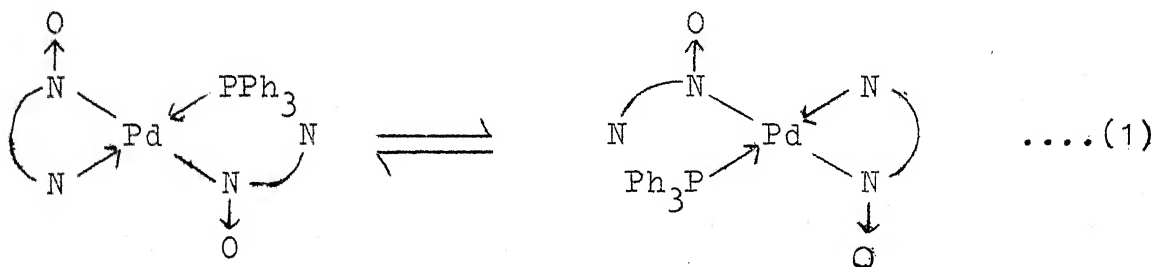
and the simplest rationalisation of the interconversion of configuration is via an S_N2 mechanism involving a transition state in which both the aao groups are chelated. A high-field shift of the methyl signal is always observed whenever the aao

chelate ring is opened by phosphines (Chapter IV). Since in $\left[(\text{Meaao})_2\text{Pd}(\text{PPh}_3)\right]$, effectively one aao chelate ring is open, the average value of δ_{CH_3} is expected to be less than that in $\text{Pd}(\text{Meaao})_2$. This is what is observed.

The Complex $\left[(\text{Meaao})_2\text{Pd}(\text{PPh}_3)_2\right]$

When a solution of $\text{Pd}(\text{Meaao})_2$ and PPh_3 (molar ratio 1:2) in benzene is concentrated to a very small volume, an orange solid crystallises out which analyses as $\left[(\text{Meaao})_2\text{Pd}(\text{PPh}_3)_2\right]$

It is tempting to assign structure III to the complex $\left[(\text{Meaao})_2\text{Pd}(\text{PPh}_3)_2\right]$ since its infrared spectrum in KBr shows no characteristic absorption of closed aao chelate ring (Fig. V.2; Table V.2) and an electronic band at 465 nm is observed in the solid state. The complex however, dissolves
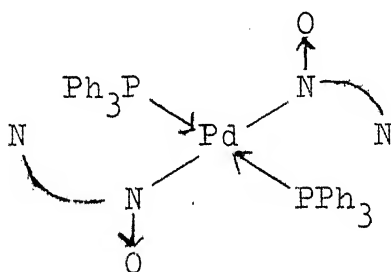
III

in benzene, chloroform and dichloromethane to give red solutions. The electronic spectrum in benzene exhibits the typical band at 500 nm with $\epsilon = 7000$. Thus III is completely converted into II in solution. This conversion is further confirmed by the room temperature pmr spectrum of III where a broad methyl signal at $\delta = 1.82$ ppm is observed.

Addition of excess PPh_3 to the solution of either $\left[(Meaao)_2Pd(PPh_3)\right]$ or $\left[(Meaao)_2Pd(PPh_3)_2\right]$ results in considerable broadening of the methyl signal with no change in chemical shift. The electronic spectrum of $\left[(Meaao)_2Pd(PPh_3)\right]$ in benzene however, remains unchanged with progressive addition of PPh_3. In solution, the reaction of PPh_3 with $Pd(Meaao)_2$ does not appear to proceed beyond the formation of $\left[(Meaao)_2Pd(PPh_3)\right]$.

C. Reactions with Tri-m-tolylphosphine and Tri-p-tolylphosphine

$Pd(Meaao)_2$ reacts with one equivalent of $P(m\text{-tol})_3$ or $P(p\text{-tol})_3$ in benzene to produce complex of the type II. Both the reactions were monitored by adding various amounts of the phosphines to solution of $Pd(Meaao)_2$ in benzene. The intense band at 500 nm reaches its limiting intensity ($\varepsilon = 7000$) when one equivalent of phosphine is added. Further addition of phosphine does not bring about any change in the electronic spectrum. No attempt was made to isolate the complexes in pure crystalline state.

D. Behavior of Tri-o-tolylphosphine and Triphenylarsine

Both $P(o\text{-tol})_3$ and $AsPh_3$ are unable to open the aao chelate ring in $Pd(Meaao)_2$. No change is detected in the electronic spectrum of $Pd(Meaao)_2$ in benzene in presence of various amounts of $P(o\text{-tol})_3$ or $AsPh_3$. Similar behavior of these two donors has already been noted in Chapter IV.

E. Complexes with Both Arylazooximato Rings Open

Complexes which contain two aao chelate rings in open-azo configuration and are stable both in solid state and in solution have been obtained by reacting $Pd(Meaao)_2$ with 1,2-bis(diphenylphosphino)ethane,(diphos) and 1-diphenylphosphino-2-diphenylarsinoethane,(arphos).

a. Reaction with Diphos

When one equivalent of diphos is added to a solution of $Pd(Meaao)_2$ in benzene, the initial green color turns orange and slowly bright orange crystals of $\left[(Meaao)_2Pd(diphos)\right]$ separate out e.g.

$$\cdots (2)$$
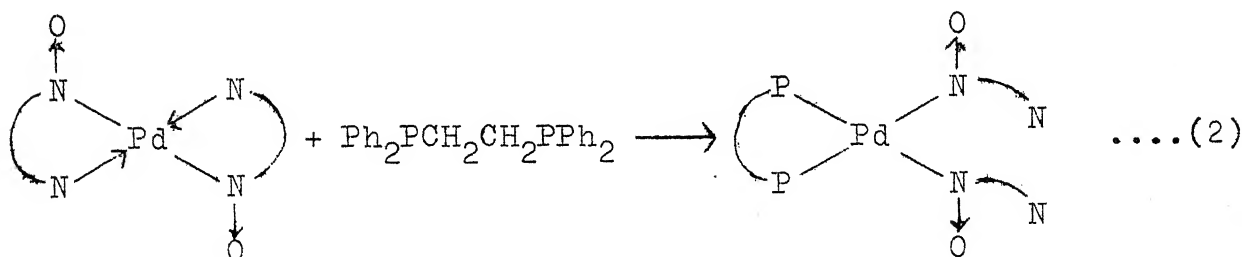
IV

The infrared vibrations of $\left[(Meaao)_2Pd(diphos)\right]$ are set out in Table V.2. Absorption around 1490 cm^{-1} confirm that the azo-ends of the aao chelate rings are open. The electronic spectrum of $\left[(Meaao)_2Pd(diphos)\right]$ exhibits bands at 450 nm and 365 nm in solid state. In chloroform, the bands appear at 415 nm ($\epsilon = 24,200$), 350 nm ($\epsilon = 36,500$), 325 nm ($\epsilon = 32,200$) and 255 nm ($\epsilon = 33,200$) (Fig. V.3). Clearly the complex

INFRARED DATA (IN KBr DISCS) OF PALLADIUM(II) COMPLEXES WITH
ARYLAZOOXIMATO CHELATE RING(S) OPEN (FREQUENCIES ARE IN cm^{-1})

Compound	ν_{C-H}	ν_{N-O}	Other Vibrations
$[(Meaao)_2 Pd(PPh_3)]$	3060(m) 2910(w)	1260(vs)	1585(w),1500(m),1490(m),1430(s),1455(w),1435(s), 1380(s),1340(s),1330(s),1200(m),1095(s),1070(m), 1040(m),1000(m),765(s),740(s),725(m),710(m), 690(s),610(m),600(s),565(m),540(s),530(s), 515(s),500(m).
$[(Meaao)_2 Pd(PPh_3)_2]$	3060(m) 2920(w)	1250(vs)	1580(w),1490(m),1480(s),1435(s),1340(s),1310(m), 1185(m),1150(m),1100(s),1070(m),1010(m),775(s), 755(s),690(s),620(s),605(s),575(s),535(s), 520(s),495(s).
$[(Meaao)_2 Pd(diphos)]$	3060(m) 2910(w)	1250(vs)	1590(w),1575(w),1505(s),1490(m),1485(s),1435(s), 1340(s),1310(m),1150(m),1100(s),1070(m),990(m), 770(s),740(s),720(s),705(s),690(s),620(m), 600(s),565(s),545(s),485(s).

Table V.2..contd.

TABLE V.2 (contd.)

Compound	ν_{C-H}	ν_{N-O}	Other Vibrations
[(Meaao)$_2$Pd(arphos)]	3050(m) 2910(w)	1255(vs)	1580(w),1500(m),1490(m),1480(s),1440(s), 1345(s),1310(m),1190(w),1100(m),1050(w), 1000(m),770(s),735(s),685(s),620(s),600(s), 565(s),535(s),485(s).
[(Meaao)Pd(azbz)(PPh$_3$)][a]	3030(m) 2920(w)	1250(vs)	1580(s),1490(m),1480(s),1455(m),1430(s), 1395(s),1340(s),1310(s),1190(s),1150(s), 1135(m),1105(m),1090(s),1060(m),1005(m), 995(s),910(m),770(s),755(s),710(s),690(s), 620(m),600(s),540(s),525(s),495(s),450(m).

w = weak; m = medium; s = strong; vs = very strong.

a azbz = orthometallated azobenzene chelate ring.
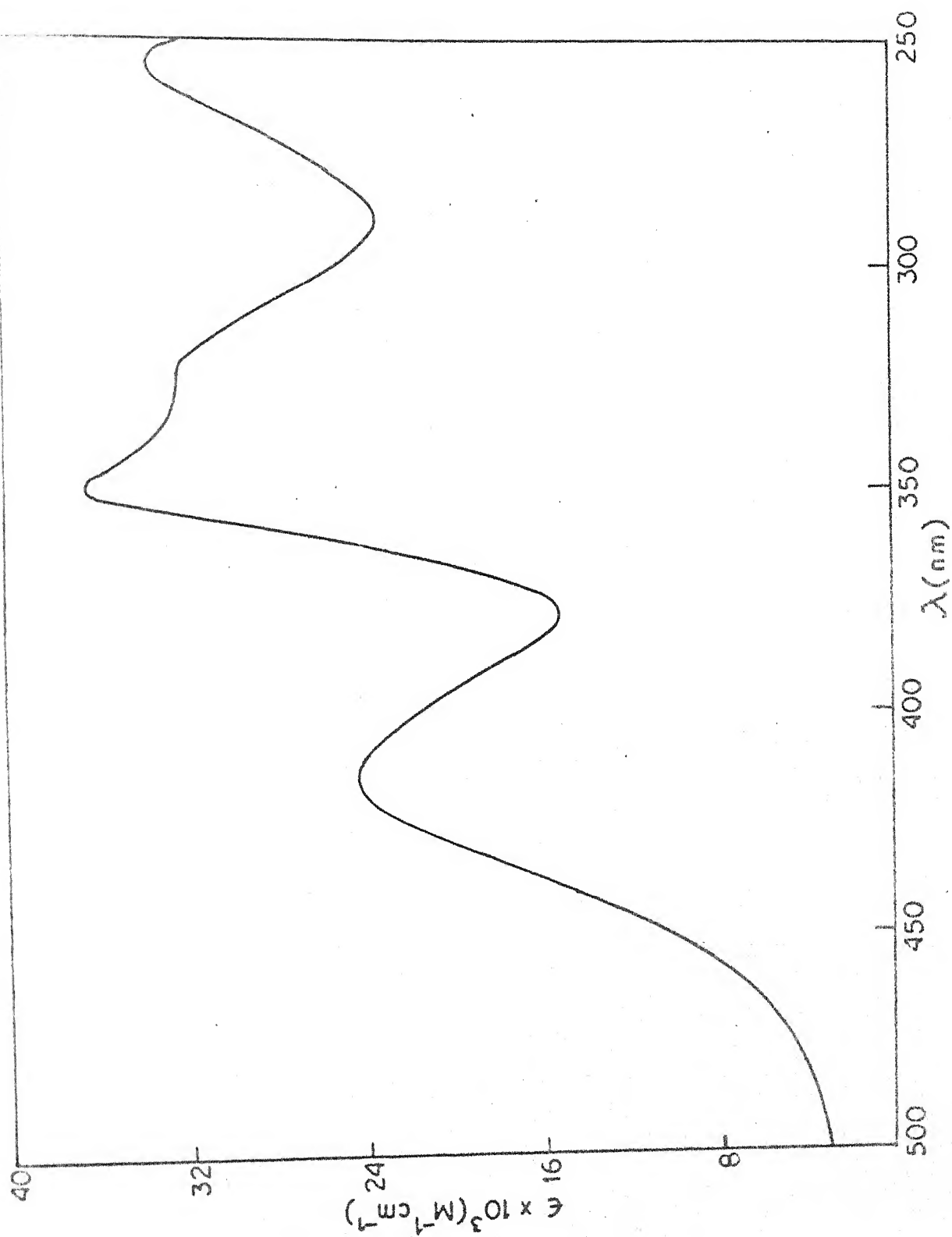
FIG.Ⅴ.3. ELECTRONIC SPECTRUM OF $[(Meaao)_2 Pd(diphos)]$ IN CHLOROFORM.

contains both the aao fragments in the open-azo configuration. The diphos chelate ring is stable enough to keep both the aao chelate rings open and structure IV is reasonably proposed for the complex $\left[(\text{Meaao})_2\text{Pd(diphos)}\right]$.

In the room temperature pmr spectrum of $\left[(\text{Meaao})_2\text{Pd(diphos)}\right]$ (Fig. V.4), the methyl signal appears at exactly the same position (δ = 1.80 ppm) as that in $\left[(\text{Meaao})\text{Pd(diphos)Cl}\right]$. The high-field shift of the methyl signal due to anisotropic diamagnetic shielding by the phenyl groups of the phosphine has been discussed in Chapter IV. The bridge CH_2 protons resonate at δ = 2.10 and 2.30 ppm ($^2J_{PH}$ = 20 Hz).

b. Reaction with Arphos

Pd(Meaao)_2 reacts with one equivalent of arphos in benzene to produce a deep red solution. Orange needles of $\left[(\text{Meaao})_2\text{Pd(arphos)}\right]$ are obtained on concentrating the solution to a small volume.

The infrared spectrum of $\left[(\text{Meaao})_2\text{Pd(arphos)}\right]$ is very much similar to that of IV (Fig. V.5; Table V.2) and the electronic spectrum in solid state exhibit no band around 500 nm. The structure of the complex, in solid state is therefore, believed to be analogous to IV.

Compared to diphos, the stability of the arphos ring is considerably reduced due to the introduction of the As center.
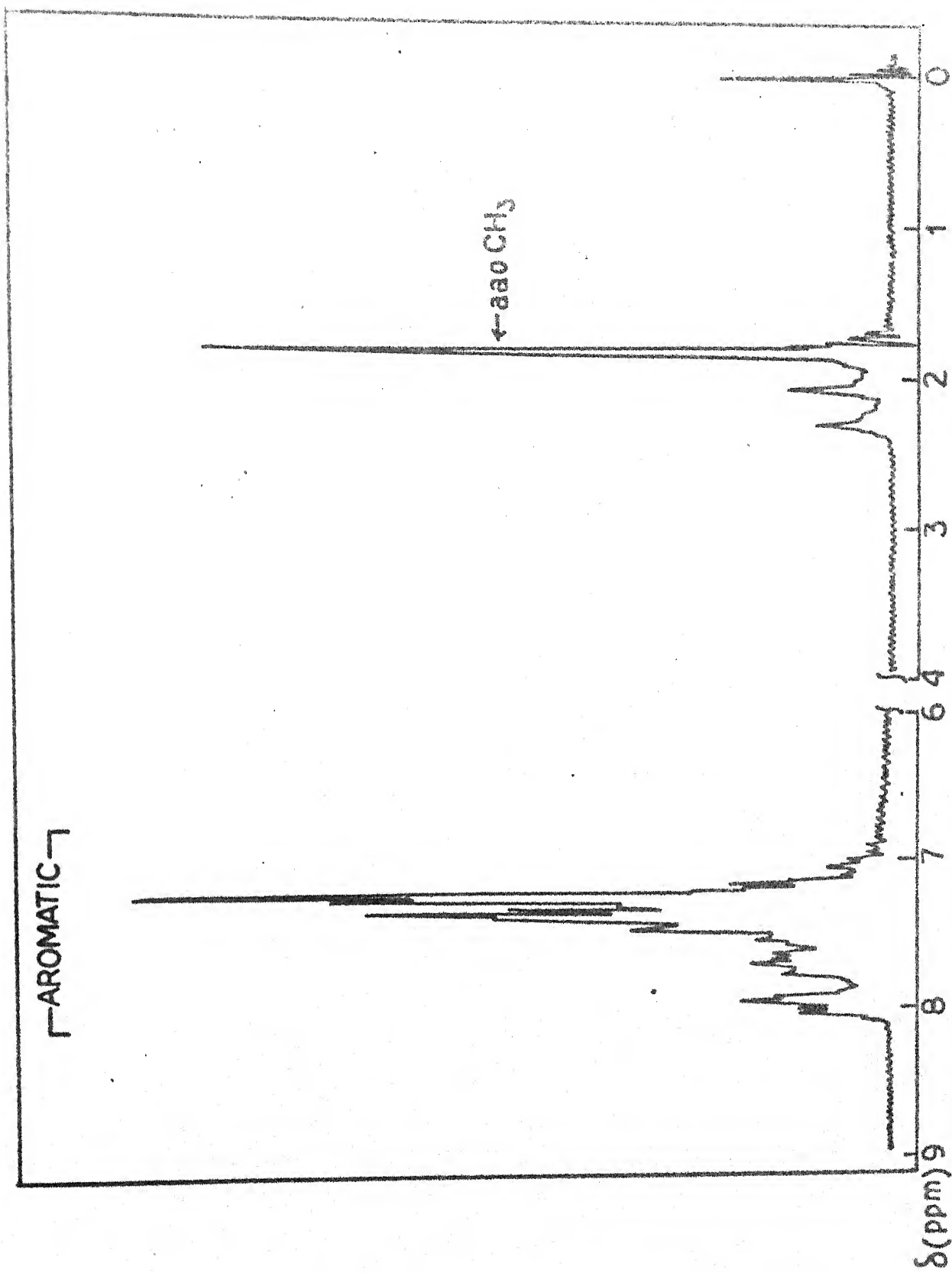
FIG Ⅴ.4 PMR SPECTRUM OF [(Meaao)$_2$ Pd(diphos)] IN CDCl$_3$.
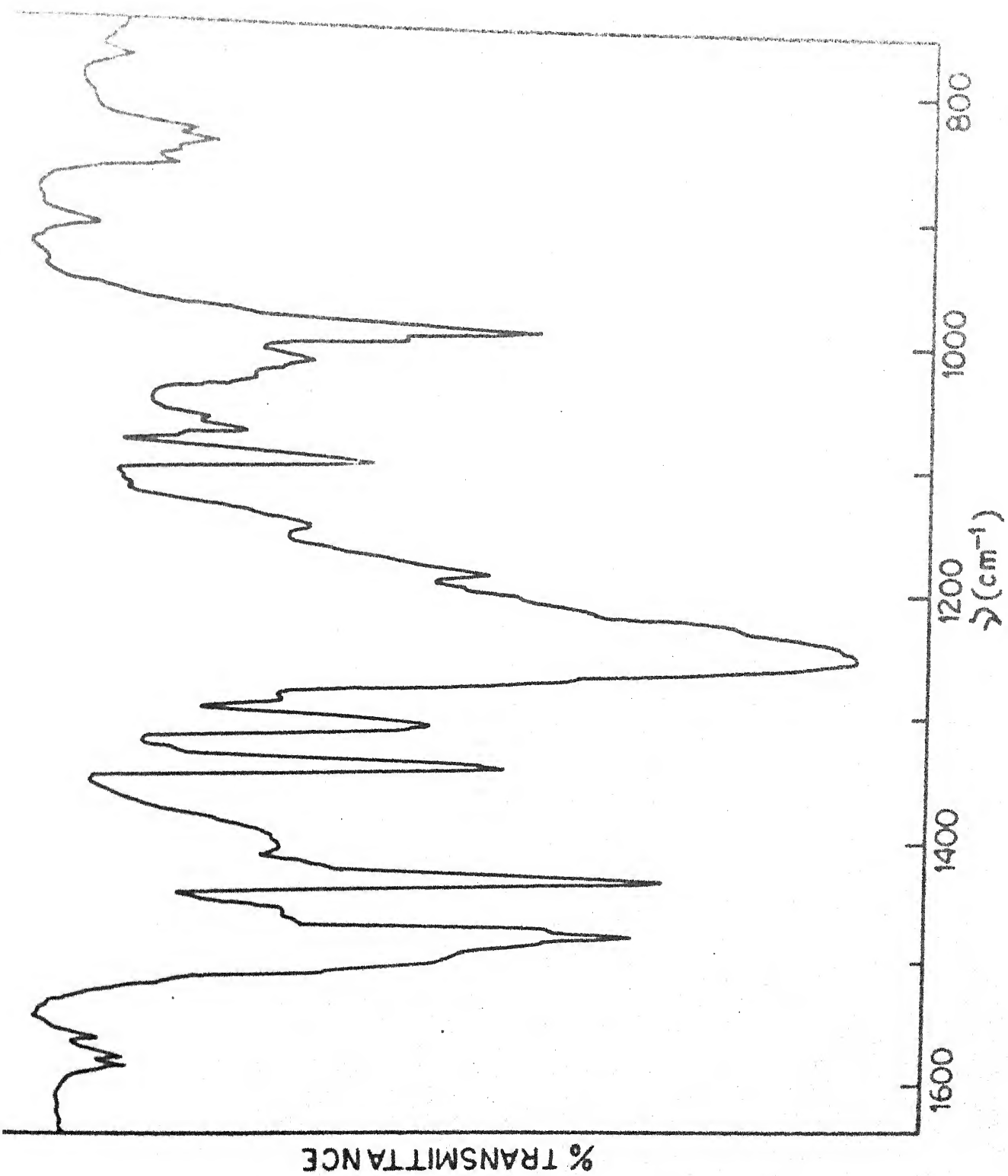
This reduction in stability is reflected in the behavior of $\left[(\text{Meaao})_2\text{Pd(arphos)}\right]$ in solution. The complex dissolves in benzene (or chloroform) to give an orange-red solution which shows weak absorption around 500 nm. It appears that in solution the As-end of the arphos chelate ring is partially opened by one of the aao fragment (which in turn completes chelation) to produce the species V.

V
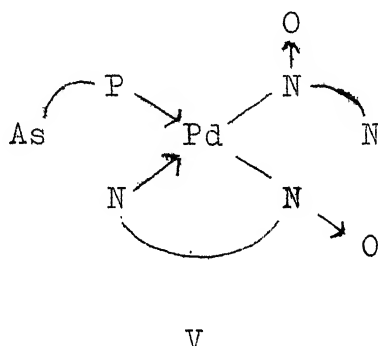
F. Reaction of the Mixed Species Pd(Meaao)(azbz) with PPh$_3$

Opening of chelate rings by PPh$_3$ is known for a few halo-bridged cyclopalladated complexes[1]. In all the cases the Pd-N bond is cleaved by PPh$_3$ whereas the Pd-C σ-bond remains unaffected. Since both the aao and the orthopalladated azo-benzene chelate rings in the mixed species Pd(Meaao)(azbz) are susceptible to attack by PPh$_3$, it was thought worthwhile to investigate the reaction of the complex with PPh$_3$.

The addition of one equivalent of PPh$_3$ to Pd(Meaao)(azbz) in benzene is accompanied by a color change from violet to orange-yellow. When the orange-yellow solution is concentrated

to small volume and hexane is added to it, maroon crystals of
$\left[(\text{Meaao})\text{Pd}(\text{azbz})(\text{PPh}_3)\right]$ are deposited.

The infrared spectrum of $\left[(\text{Meaao})\text{Pd}(\text{azbz})(\text{PPh}_3)\right]$
(Table V.2) clearly points out that the aao chelate ring is open
(structure VIII, C-N is orthopalladated azobenzene chelate ring).
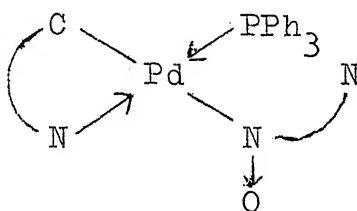
VIII

The orange solution of the complex in benzene (or chloroform) however, turns red on dilution. The electronic spectrum
of $\left[(\text{Meaao})\text{Pd}(\text{azbz})(\text{PPh}_3)\right]$ in benzene exhibit weak absorption at
550 nm. It appears that in solution the complex is partially
converted to Pd(Meaao)(azbz) due to dissociation of PPh$_3$.

The room temperature pmr spectrum of $\left[(\text{Meaao})\text{Pd}(\text{azbz})(\text{PPh}_3)\right]$
(Fig. V.6) provides additional support to structure VIII. The
methyl signal of the aao fragment appears at δ = 1.33 ppm
(δ_{CH_3} for Pd(Meaao)(azbz) = 2.4 ppm). This high-field shift of
the methyl signal confirms that in $\left[(\text{Meaao})\text{Pd}(\text{azbz})(\text{PPh}_3)\right]$, the
aao fragment exists in the open-azo configuration. Moreover,
since the methyl signal is quite sharp at room temperature
there seems to be little exchange between open and closed
chelate rings.

AROMATIC
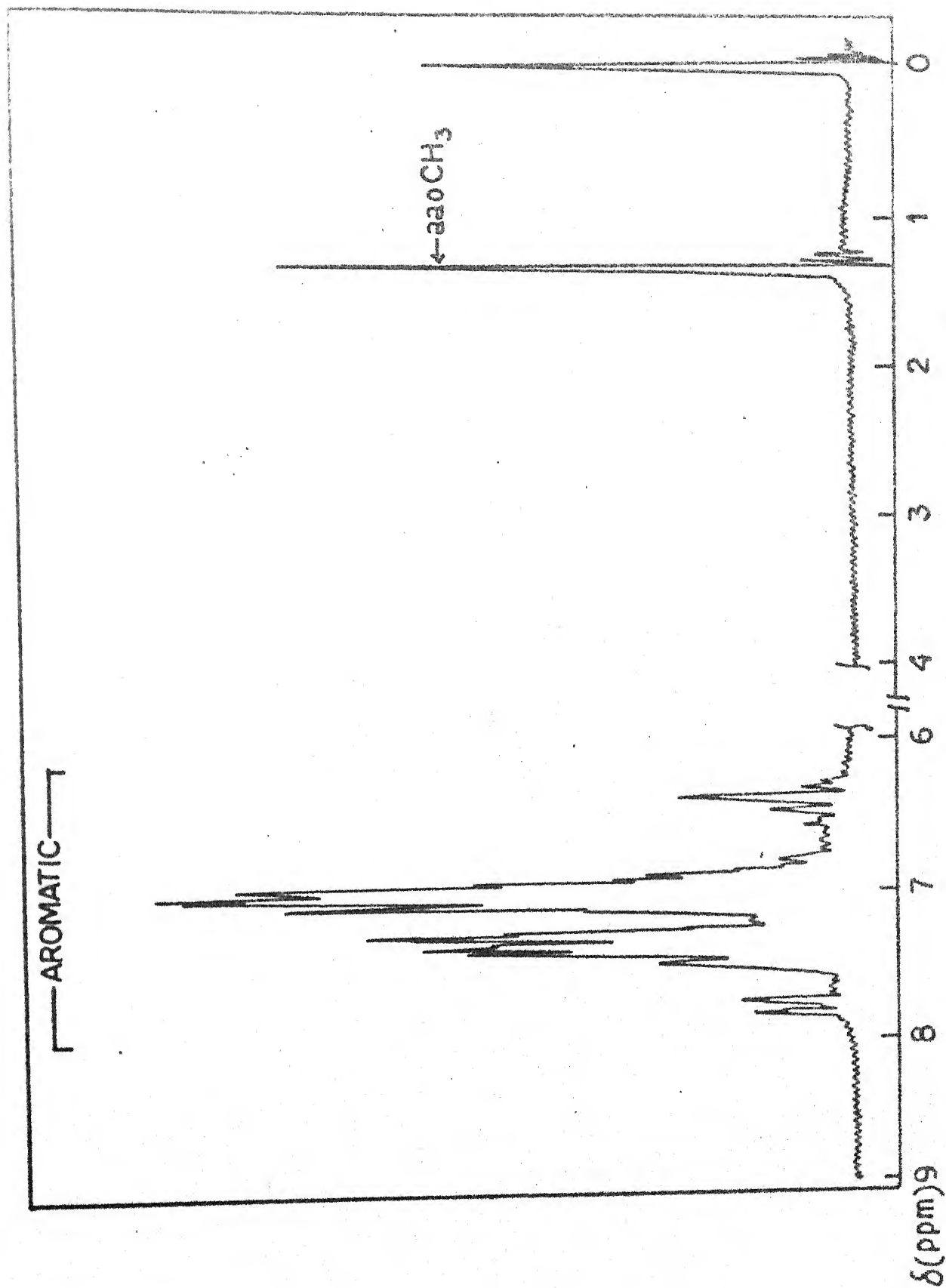
←aaoCH₃

FIG.⨉.6. PMR SPECTRUM OF [(Meaao)Pd(azbz)(PPh₃)] IN CDCl₃.

δ(ppm)9

G. Reactions of Pd(Raao)$_2$ with HCl

It has already been demonstrated in Chapter IV that HCl opens the aao chelate ring at the oxime-end with concomitant protonation of the oximato group. The reactions of HCl with the bis-arylazooximates of palladium(II) provide further confirmation to this finding. Passage of HCl gas through solutions of Pd(Raao)$_2$ (R = Me, Ph, p-tol) in benzene (or chloroform) brings about a sharp color change from green to orange-red. When the orange-red solutions are poured into water or treated with a base, the bis-complexes are regenerated i.e.

$$\text{Pd(Raao)}_2 \quad \underset{\text{mild bases}}{\overset{\substack{\text{bz or chl} \\ \text{pass HCl}}}{\rightleftharpoons}} \quad \text{Orange-red solutions} \quad \text{....(3)}$$
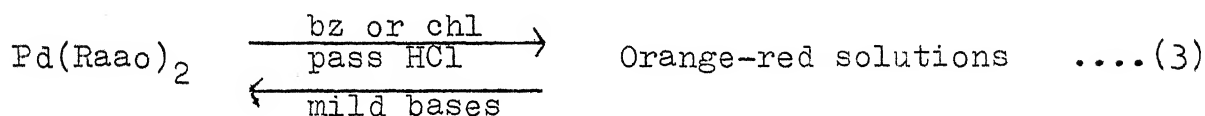
R=Me,Ph,p-tol

Addition of hexane to the orange-red solutions, however, precipitates bright red crystals of Pd$_2$(HRaao)$_2$Cl$_4$, VI (R = Me, Ph, p-tol) and one mol of respective arylazooxime per Pd atom is
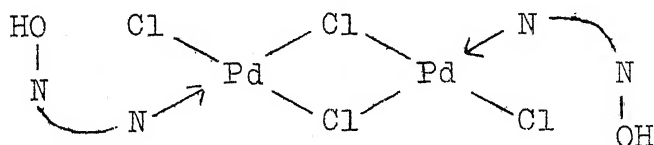
VI

left in the mother liquor. As already stated in Chapter IV, the complexes VI are quite unstable and are converted to the

halo-bridged arylazooximes $Pd_2(Raao)_2Cl_2$ soon after these are
separated from the mother liquor. Infrared spectra (in KBr),
electronic spectra (in benzene) and the quantitative conversion
of VI to $Pd_2(Raao)_2Cl_2$ have been used for the characterisation
of the complexes VI (R = Me, Ph, p-tol). The infrared data of
$Pd_2(HMeaao)_2Cl_4$ and $Pd_2(HPhaao)_2Cl_4$ are already collected in
Table IV.6 (Chapter IV). The infrared absorption frequencies of
$Pd_2(H\ p\text{-}tolaao)_2Cl_4$ are set out below.

  3020(s,br), 1600(s), 1575(s), 1500(m), 1480(m), 1455(s),
  1420(s), 1380(s), 1320(m), 1290(m), 1250(s), 1180(s), 1160(m)
  1152(m), 1132(s), 1120(s), 1075(m), 1010(m), 830(m), 820(s),
  780(s), 770(s), 755(s), 715(m), 710(s), 685(s), 650(s),
  610(m), 550(m), 485(s) and 355(s).

Reactions of the bis-arylazooximes with HCl gas thus
result in rejection of one mol of arylazooxime per Pd atom and
generation of VI. This reaction may proceed via an unstable
intermediate VII which dimerises with the formation of VI. In
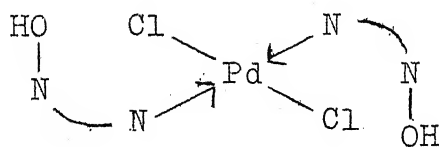
VII

an attempt to isolate the species VII with R = Ph, $Pd(PhCN)_2Cl_2$
was allowed to react with two equivalents of HPhaao in dry

benzene when a deep red solution was obtained. However, the only
isolable species from the red solution was VI (R=Ph) which
slowly crystallised out on keeping.

It is interesting to note that since the orange-red
solutions (produced by reacting the bis-complexes with HCl in
benzene) contain VI and free arylazooxime ligands in the molar
ratio 1:2, addition of water or other mild bases brings about
two consecutive reactions namely conversion of VI to $Pd_2(Raao)_2Cl$
followed by the conversion of $Pd_2(Raao)_2Cl_2$ to $Pd(Raao)_2$. Also
since VI is readily converted to the halo-bridged arylazooxi-
mates, HCl gas can be used for the conversion of $Pd(Raao)_2$ to
$Pd_2(Raao)_2Cl_2$.

H. Oxidative Addition of Arylazooximes to $\left[Pd(PPh_3)_4\right]$

The oxidative addition of molecules of the type XY to
tetrakis(triphenylphosphine)palladium(O) is a well studied
reaction. $\left[Pd(PPh_3)_4\right]$ reacts with alkyl halides, acetyl
chloride, ethylchloroformate, methallyl chloride and
iodobenzene[2] to yield complexes of the type trans-$\left[(PPh_3)_2Pd(R)X\right]$
Reaction of chloroolefins with $\left[Pd(PPh_3)_4\right]$ in benzene leads to
Pd(II)-σ-alkenyl complexes[3]. Addition of benzoyl chloride to a
suspension of $\left[Pd(PPh_3)_4\right]$ in benzene[4] produces
<u>trans</u>-$\left[(PPh_3)_2Pd(CH_2C_6H_5)Cl\right]$. Unstable hydride complexes of
palladium have been synthesised by the action of HCl on
$\left[Pd(PPh_3)_4\right]$ and other phosphine complexes of zerovalent

palladium[5]. These interesting reactions stimulated the idea of investigating the oxidative addition of arylazooximes to $\left[Pd(PPh_3)_4\right]$.

The oxidative addition of one equivalent of arylazooxime to $\left[Pd(PPh_3)_4\right]$ is expected to give rise to a Pd(II) hydride complex. Since the hydride complexes of palladium are unstable thermally as well as in acidic or basic medium and require very low temperature for their syntheses[5], such species were not investigated. Instead, attempts were made to characterise the reaction products of the oxidative addition of two mols of arylazooxime to one mol of $\left[Pd(PPh_3)_4\right]$. The reaction of phenylazoacetaldoxime with $\left[Pd(PPh_3)_4\right]$ is described here.

When a suspension of $\left[Pd(PPh_3)_4\right]$ in dehydrated ethanol is stirred with two equivalents of phenylazoacetaldoxime in nitrogen atmosphere, the entire amount of $\left[Pd(PPh_3)_4\right]$ dissolves slowly (24 hrs) to produce an orange-red solution. As the stirring is continued, orange crystals of $\left[(Meaao)_2Pd(PPh_3)_2\right]$ separates out of the orange-red solution. The overall reaction can be written as

$$\left[Pd(PPh_3)_4\right] + 2\ HMeaao \xrightarrow[\text{N}_2\ \text{atoms}]{\text{EtOH}}$$

III
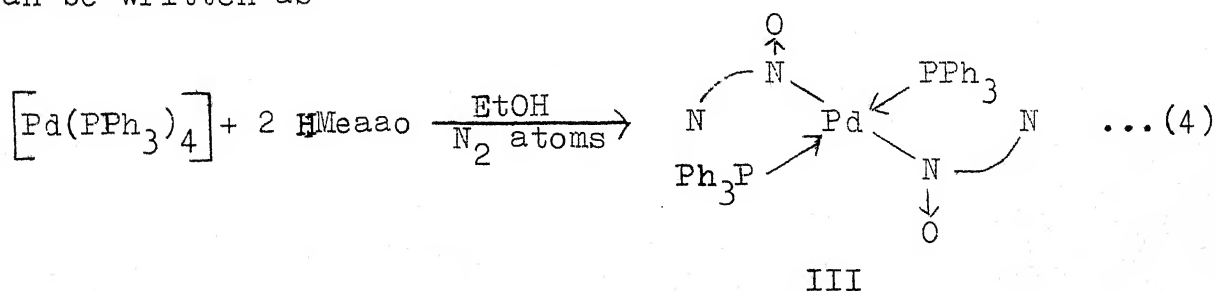
The dissociable oxime protons of the arylazooximes in reaction (4) are likely to be lost as dihydrogen. Since

$\left[(PPh_3)_2Pd(H)Cl\right]$ reacts with HCl to produce $\left[(PPh_3)_2PdCl_2\right]$ and H_2, it is reasonable to postulate that the intermediate hydride $\left[(Meaao)Pd(H)(PPh_3)_2\right]$ reacts with HMeaao to yield $\left[(Meaao)_2Pd(PPh_3)_2\right]$ and dihydrogen.

Benzene was also tried as the solvent for the reaction-(4). Addition of two equivalents of HMeaao to $\left[Pd(PPh_3)_4\right]$ in benzene (nitrogen atmosphere) results in a deep red solution. However, attempts to isolate any crystalline solid from this red solution failed.

Studies on the oxidative addition of arylazooximes with R = aryl to $\left[Pd(PPh_3)_4\right]$ are in progress.

I. Oxidation of Pd(Raao)$_2$ with Halogens

In this section the results of preliminary investigation on the oxidation of the bis-arylazooximates Pd(Raao)$_2$ with dichlorine and dibromine are reported.

Oxidation of square-planar Pd(II) complexes to octahedral Pd(IV) complexes with halogens in chloroform or dichloromethane is known for a few cases[6]. Bis(dimethylglyoximato)palladium(II) and bis(diphenylglyoximato)palladium(II) undergo oxidation with halogens in orthodichlorobenzene to produce complexes of the type $\left[Pd(dmg)_2X\right]$ and $\left[Pd(dpg)_2X\right]$. The compounds have been described as inclusion type molecular complexes stabilised by charge transfer interactions[7]. The properties and structures

of these species have been discussed quite thoroughly[8]. The compounds are diamagnetic and do not give rise to esr signals though reports on the presence of paramagnetic impurities (caused by lattice defects where distinct paramagnetic units cannot pair their spins with neighbouring units) are there[9]. A linear chain mixed valence solid of stoichiometry $Pd(dmg)_2I$ has also been reported[10]. The reaction of halogens with the bis-arylazooximates seems to be quite promising in this background.

Solution of $Pd(Meaao)_2$ in benzene (or chloroform) on exposure to dichlorine for a short time or on treatment with one equivalent of dibromine, exhibits a color change from green to red. When the red solution is concentrated to small volume and ethanol is added, violet crystals of di-μ-halobis[phenylazo-acetaldoximatopalladium(II)] are deposited. In case of $Pd(Raao)_2$ with R = aryl, the red solutions produced by reaction with halogens are thermally unstable and the halo-bridged complexes start depositing out while concentrating the solutions to small volumes. Addition of ethanol quickens and completes the precipitation of $Pd_2(Raao)_2X_2$, (R = aryl).

Excess halogens in all the cases have been found to bring about complicated reactions leading to formation of PdX_2 and other organic compounds. No attempt has been made to characterise the organic compounds.

The nature of the species present in the red solutions
is not yet definitively established. Most possibly the initial
reaction is an oxidation reaction which leads to the formation
of unstable Pd(IV) species in solution. The presence of unstable
Pd(IV) species in the red solutions is postulated in analogy with
complexes of the type $\left[(\text{Raao})_2\text{Pt}^{IV}\text{X}_2\right]$ which have been isolated
from similar red solutions produced in the reactions between
Pt(Raao)$_2$ and halogens (Chapter VI). Moreover, the infrared
spectra of the red solutions (in chloroform) produced by the
action of dichlorine on Pd(Meaao)$_2$ and Pt(Meaao)$_2$ are very much
similar. Pd(IV) species are known to be quite unstable and hence
it is possible that the reaction conditions are not suitable
enough for the isolation of such species.

At present, the role of ethanol is not well understood.
It is suspected that ethanol reduces the Pd(IV) species in
solution i.e.

$$\text{Pd(Raao)}_2 + \text{X}_2 \xrightarrow{\text{bz}} \left[(\text{Raao})_2\text{PdX}_2\right] \xrightarrow{\text{EtOH}} \text{Pd}_2(\text{Raao})_2\text{X}_2$$

$$\text{red solution} \qquad \qquad \dots(5)$$
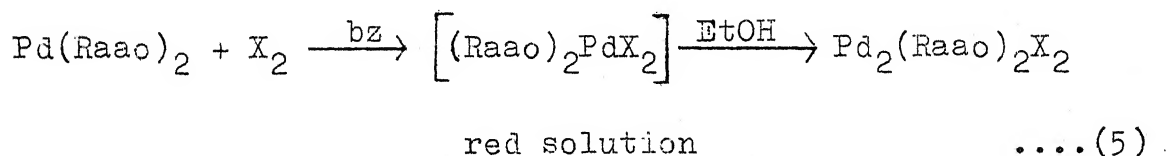
Evidences in favor of this proposition will be available if the
products of the reduction step could be characterised. Investi-
gation in this direction has already been initiated. Apart from
functioning as a reducing agent, ethanol acts as a precipitating
agent for the halo-bridged complexes also.

Some Properties of the Red Solutions Produced from Pd(Meaao)$_2$ and X$_2$ (X = Cl, Br)

The dark red solutions are diamagnetic and do not contain free halogen. The methyl signal of the aao group appears at δ = 2.33 ppm and 2.43 ppm for the chloro- and bromo-species respectively (δ_{CH_3} for Pd(Meaao)$_2$ = 2.13 ppm). The room temperature pmr spectrum of the red solution obtained from the 1:1 reaction between Pd(Meaao)$_2$ and Br$_2$ is shown in Fig. V.7.

V.3   EXPERIMENTAL SECTION

A. Preparation of Complexes

a. $\left[(\text{Meaao})_2\text{Pd(PPh}_3)\right]$

A solution containing 215 mg (0.5 mmol) of bis(phenyl-azoacetaldoximato)palladium(II) and 131 mg (0.5 mmol) of triphenylphosphine in 20 ml of benzene was slowly evaporated to dryness under low pressure when a violet residue was left. The residue on recrystallisation from boiling hexane yielded 250 mg (70%) of pure crystalline product.
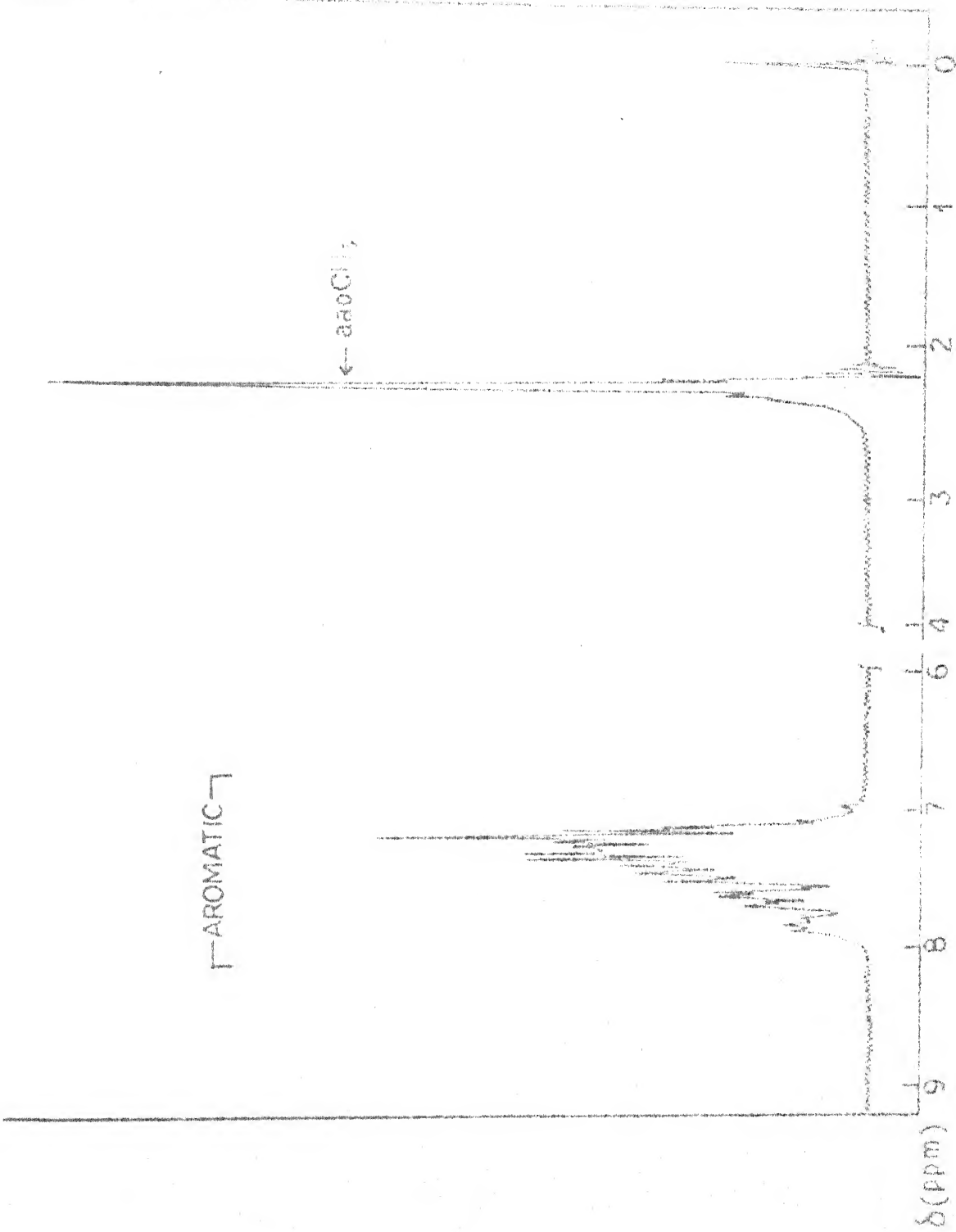
FIG. IV. 7. PMR SPECTRUM OF THE RED SOLUTION OBTAINED FROM THE

[H] REACTION BETWEEN Pd(MeCOO)₂ AND PPh₃ IN CDCl₃.

b. $\left[(Meaao)_2Pd(PPh_3)_2\right]$

A solution of 524 mg (2 mmol) of triphenylphosphine in 15 ml of benzene was mixed with a solution of 430 mg (1 mmol) of bis(phenylazoacetaldoximato)palladium(II) in 15 ml of benzene. The resulting orange-red solution was then allowed to evaporate slowly in vacuum. Orange crystals of $\left[(Meaao)_2Pd(PPh_3)_2\right]$ started separating out when the volume of the solution was $\sim$ 5 ml. The crystals were collected by filtration, washed with hexane (minimum volume) and finally dried in vacuum (yield $\sim$ 60%).

c. $\left[(Meaao)_2Pd(diphos)\right]$

To a solution of 215 mg (0.5 mmol) of bis(phenylazo-acetaldoximato)palladium(II) in 20 ml of benzene was added with stirring a solution of 200 mg (0.5 mmol) of 1,2-bis(diphenyl-phosphino)ethane, (diphos) in 10 ml of benzene. The initial green color changed to orange and as the stirring was continued the complex $\left[(Meaao)_2Pd(diphos)\right]$ separated out as an orange solid. The solid was filtered, washed with benzene and finally recrystallised from chloroform (yield $\sim$ 65%).

d. $\left[(Meaao)_2Pd(arphos)\right]$

A solution containing 221 mg (0.5 mmol) of 1-diphenyl-phosphino-2-diphenylarsinoethane, (arphos) in 10 ml of benzene

was added to a solution containing 215 mg (0.5 mmol) of
bis(phenylazoacetaldoximato)palladium(II) in 20 ml of benzene.
The deep red solution thus resulted was slowly concentrated to
$\sim$ 5 ml when orange needles of $\left[(Meaao)_2Pd(arphos)\right]$ were
deposited. The crystals were collected by filtration, washed
with benzene (minimum volume) and dried in vacuum (yield $\sim$ 60%).

e. $\left[(Meaao)Pd(azbz)(PPh_3)\right]$

225 mg (0.5 mmol) of Pd(Meaao)(azbz) was dissolved in
25 ml of benzene and to it was added a solution of 131 mg
(0.5 mmol) of triphenylphosphine in 10 ml of benzene when an
orange solution was obtained. The solution was then concen-
trated to small volume ($\sim$ 5 ml) under low pressure. On
addition of 10 ml of hexane to the concentrated solution,
maroon crystals of $\left[(Meaao)Pd(azbz)(PPh_3)\right]$ were deposited.
They were collected by filtration, washed with hexane and
finally dried in vacuum (yield $\sim$ 70%).

f. Generation of $Pd_2(HRaao)_2Cl_4$, (R = Me, Ph, p-tol) Species

The procedure for the generation of $Pd_2(HMeaao)_2Cl_4$ is
described below.

About 250 mg of bis(phenylazoacetaldoximato)palladium(II)
was dissolved in 20 ml of benzene and a slow stream of dry

HCl gas was allowed to pass through the solution. As a few bubbles of HCl were passed, the deep green solution turned orange-red and red crystals of $Pd_2(HMeaao)_2Cl_4$ were deposited when hexane ($\sim$ 10 ml) was added to it.

$Pd_2(HPhaao)_2Cl_4$ and $Pd_2(Hp\text{-}tolaao)_2Cl_4$ were obtained following similar procedure.

g. Oxidative Addition of HMeaao to $\left[Pd(PPh_3)_4\right]$

Tetrakis(triphenylphosphine)palladium(0), $\left[Pd(PPh_3)_4\right]$ was synthesised as described in the literature[11].

To a suspension of 231 mg (0.2 mmol) of $\left[Pd(PPh_3)_4\right]$ in 20 ml of dehydrated ethanol stirring under nitrogen was added a solution containing 66 mg (0.4 mmol) of phenylazoacetaldoxime in 10 ml of dehydrated ethanol. As the stirring was continued, the color of the solution turned orange-red and after 24 hrs, the entire amount of $\left[Pd(PPh_3)_4\right]$ dissolved to give a dark orange-red solution. Orange crystals of $\left[(Meaao)_2Pd(PPh_3)_2\right]$ were deposited on further stirring. The crystals were collected by filtration, washed with dehydrated ethanol (all the operations were carried out in nitrogen atmosphere) and dried in vacuum (yield $\sim$ 75%).

h. Oxidation of $Pd(Raao)_2$ with Halogens

(i) Oxidation with Dichlorine

Bis(phenylazoacetaldoximato)palladium(II) was oxidised with dichlorine in the following way.

About 200 mg of $Pd(Meaao)_2$ was dissolved in 15 ml of chloroform and the green solution was carefully exposed to dichlorine for ∿5 seconds with constant stirring. The solution was removed from dichlorine atmosphere immediately after it turned deep red. This red solution was directly used for infrared measurements.

For pmr studies, the red solution was obtained by exposing a solution of $Pd(Meaao)_2$ in $CDCl_3$ to dichlorine.

$Pd(Phaao)_2$ and $Pd(\underline{p}\text{-tolaao})_2$ were oxidised following similar procedure.

(ii) Oxidation with Dibromine

The oxidation of bis(phenylazoacetaldoximato)palladium(II) with dibromine is described below.

215 mg (0.5 mmol) of $Pd(Meaao)_2$ was dissolved in 20 ml of chloroform and to it was added with constant stirring a solution of 80 mg (0.5 mmol) of dibromine in 2 ml of chloroform. The green solution turned red but no turbidity was observed. This red solution was used for infrared measurements.

For pmr studies, $CDCl_3$ was used as the solvent for the oxidation reaction.

$Pd(Phaao)_2$ and $Pd(\underline{p}-tolaao)_2$ were oxidised with dibromine in analogous manner.

Benzene can also be used as a solvent for all these reactions.

The reactions with excess halogens and methods of obtaining $Pd_2(Raao)_2X_2$ complexes from the red solutions have already been discussed in Chapter II Section II.3.A.c(iv).

B. Characterisation of Complexes

This was done by C, H, N microanalysis and metal analysis. Characterisation data for the complexes are collected in Table V.3.

C. Physical Measurements

a. Infrared Spectra

Details are given in Chapter II.

b. Electronic Spectra

Details are given in Chapter II.

c. Proton Magnetic Resonance Spectra

Details are given in Chapter II.

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CHARACTERISATION DATA OF PALLADIUM(II) COMPLEXES

Compound	MP°C a,b	% C Calc.	Found	% H Calc.	Found	% N Calc.	Found	% Pd Calc.	Found
[(Meaao)$_2$Pd(PPh$_3$)]	85–87	58.90	58.87	4.51	4.60	12.12	12.18	15.36	15.40
[(Meaao)$_2$Pd(PPh$_3$)$_2$]	95–105	65.35	65.28	4.85	4.90	8.79	8.74	11.14	11.24
[(Meaao)$_2$Pd(diphos)]	191	60.81	60.78	4.86	4.79	10.13	10.27	12.84	12.80
[(Meaao)$_2$Pd(arphos)]	155	57.74	57.80	4.62	4.59	9.62	9.61	12.19	12.08
[(Meaao)Pd(azbz)(PPh$_3$)]	157	64.08	64.12	4.53	4.48	9.83	9.90	14.95	15.11

a All melting points reported in this table are uncorrected.

b All the complexes melt with decomposition.

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CHAPTER VI

ARYLAZOOXIMATES OF PLATINUM : PRELIMINARY INVESTIGATION

CHAPTER VI

ARYLAZOOXIMATES OF PLATINUM : PRELIMINARY INVESTIGATION

Abstract: A brief report of the preliminary investigation on
the chemistry of the arylazooximates of platinum is presented.
One halo-bridged arylazooximate namely $Pt_2(Meaao)_2Cl_2$ has been
synthesised by boiling $PtCl_2$ with HMeaao in dehydrated ethanol.
The other procedures of generating halo-bridged species are not
applicable for the synthesis of halo-bridged platinum arylazo-
oximates. Since $Pt_2(Meaao)_2Cl_2$ exhibits ν_{N-O} at 1290 cm^{-1} and
an intense electronic band at 550 nm (ϵ = 5000 per Pd atom),
the structure of the complex is believed to be similar to its
palladium analogue. Amines (am) like pyridine and aniline
undergo facile bridge-cleavage reactions to produce
$[(Meaao)Pt(am)Cl]$ complexes. The bis-complexes $Pt(Raao)_2$,
R = Me, Ph, are formed in the slow reaction between K_2PtCl_4
and HRaao in aqueous ethanol. These complexes exhibit strong
electronic bands ($\epsilon \sim 6000$) in unusually low energy region
($\sim$ 1080 nm). $Pt(Meaao)_2$ gives rise to well defined epr signal
due to the presence of small amount of paramagnetic impurity.
With two equivalents of triphenylphosphine (PPh_3), $Pt(Meaao)_2$
produces $[(Meaao)_2Pt(PPh_3)_2]$ in which both the arylazooximato

(aao) fragments exist in open-azo configuration in solid state (ir data). In solution, $[(Meaao)_2Pt(PPh_3)_2]$ partially dissociates into $[(Meaao)_2Pt(PPh_3)]$ and PPh_3. When reacted with one equivalent of $Ph_2PCH_2CH_2PPh_2$ (diphos) in benzene, $Pt(Meaao)_2$ yields $[(Meaao)_2Pt(diphos)]$. The infrared spectrum (in KBr) and the high-field shift of the methyl signal of the aao fragments indicate that in $[(Meaao)_2Pt(diphos)]$, the aao fragments remain open (at the azo-end) both in solid state and in solution.

The oxidative addition of two mols of HMeaao to $[Pt(PPh_3)_4]$ in dehydrated ethanol leads to the formation of $[(Meaao)_2Pt(PPh_3)_2]$. $Pt(Meaao)_2$ is oxidised by dichlorine and dibromine in benzene to the deep red diamagnetic $[(Meaao)_2PtX_2]$ complexes. Since only one Pt-X stretching vibration is observed, the $[(Meaao)_2PtX_2]$ complexes are believed to have a trans-configuration. Passage of HCl gas through solution of $[(Meaao)_2Pt(PPh_3)_2]$ in benzene produces trans- $[(PPh_3)_2PtCl_2]$. $Pt(Meaao)_2$ when reacted with PPh_3 and HCl, in any order, also yields trans- $[(PPh_3)_2PtCl_2]$.

VI.1   INTRODUCTION

The fascinating chemistry of the halo-bridged and bis-arylazooximates of palladium prompted investigation on the chemistry of the corresponding platinum analogues. In this chapter, the report of preliminary investigation on the reactions of platinum species primarily with phenylazoacetald-oxime is briefly presented. Reactions with phenylazobenzaldoxime are alluded to at several points.

VI.2   RESULTS AND DISCUSSION

A. Di-μ-chlorobis $\left[\text{phenylazoacetaldoximatoplatinum(II)}\right]$: Synthesis and Structure

In aqueous ethanol, the reaction of arylazooximes with K_2PtCl_4 is entirely different from that with K_2PdCl_4. No immediate reaction is evident when an ethanolic solution of an arylazooxime is added to K_2PtCl_4 in water. On prolonged stirring (48 hrs), a black solid separates out from the reaction mixture. Addition of ethanol to the solution of the black solid in chloroform deposits shinning crystals of $Pt(Raao)_2$ (vide infra) The product in this reaction is always the bis-complex irres-pective of the molar ratio of HRaao and Pt. The benzonitrile complex $Pt(PhCN)_2Cl_2$ undergoes a slow reaction (stirring for

100 hrs) with arylazooximes (molar ratio 1:1) in ethanol (or benzene) to produce $Pt(Raao)_2$ in low yield. Under no condition was it possible to obtain the desired halo-bridged species by the above two routes.

$PtCl_2$ does not appear to react with arylazooximes (molar ratio 1:1) in 95% ethanol either at room temperature or on boiling. However, when dehydrated ethanol is used as the solvent, a slow reaction occurs between $PtCl_2$ and phenylazo-acetaldoxime. The characteristic purple color of the halo-bridged arylazooximate develops on heating the mixture to reflux. After 48 hrs, $Pt_2(Meaao)_2Cl_2$ is obtained in 20% yield.

$$2\ PtCl_2 + 2\ HMeaao \longrightarrow Pt_2(Meaao)_2Cl_2 + 2\ HCl \quad \ldots\ldots(1)$$
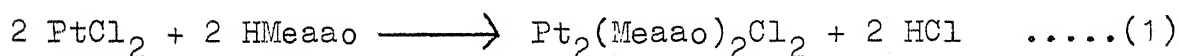
Unlike phenylazoacetaldoxime, the reaction of phenylazobenzald-oxime with $PtCl_2$ in boiling dehydrated ethanol leads to a green solution. No chloro-bridged species is formed in this reaction.

Di-μ-chlorobis $\left[\text{phenylazoacetaldoximatoplatinum(II)}\right]$, is a violet crystalline solid which is soluble in benzene, chloroform and dichloromethane.

Physical Data

As expected the infrared spectrum of $Pt_2(Meaao)_2Cl_2$ (Fig. VI.1) is very similar to that of $Pd_2(Meaao)_2Cl_2$. ν_{N-O} appears at 1290 cm^{-1} which is suggestive of the binding of the
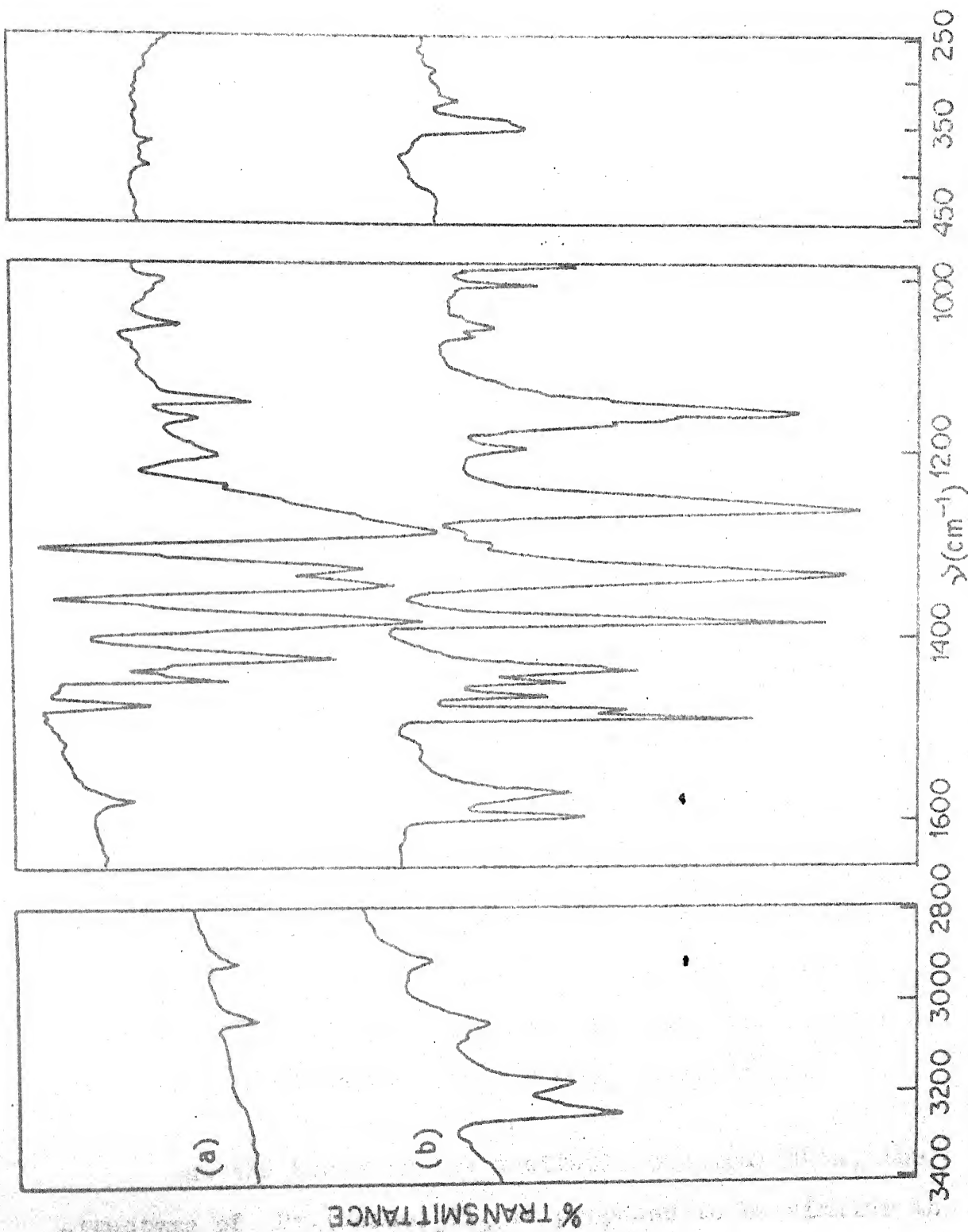
FIG. VI. 1 PARTIAL INFRARED SPECTRA OF (a) $Pt_2(Meaao)_2Cl_2$ AND (b) $\left[(Meaao)Pt(NH_2C_6H_5)Cl\right]$ IN KBr (DISC).

metal at oxime nitrogen (five-membered chelate ring) with
consequent stabilisation of the nitrone structure. Other
infrared vibrations are listed in Table VI.1.

The electronic spectrum of $Pt_2(Meaao)_2Cl_2$ in benzene
exhibits an intense band at 550 nm with extinction coefficient
of 5000 per Pt atom. As it has been pointed out in Chapter II,
this band is characteristic of the moiety I and is expected to

$$H_3C-C \diagdown \underset{\overset{\displaystyle \|}{N}}{\overset{N=N}{\diagup}} \diagdown \underset{\overset{\displaystyle \downarrow}{O}}{M} \diagup Ar$$
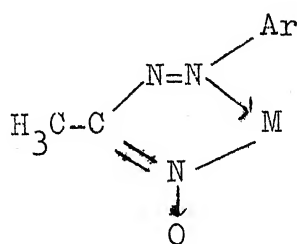
I

M = Pd, Pt

be originating from a metal $\longrightarrow$ ligand (M $\longrightarrow$ L) charge
transfer transition. The same band is observed in the bridge-
split products of the type $\left[(Meaao)Pt(Donor)Cl\right]$ (_vide infra_)
where the moiety I is present. It is significant that there
is a red shift of this band as one goes from $Pd_2(Meaao)_2Cl_2$
(λ = 535 nm) to $Pt_2(Meaao)_2Cl_2$ (λ = 550 nm). This red
shift falls in line with the M $\longrightarrow$ L assignment.

On the basis of the available physical data, the
structure of $Pt_2(Meaao)_2Cl_2$ is proposed to be similar to

INFRARED DATA OF $Pt_2(Meaao)_2Cl_2$ AND RELATED BRIDGE-SPLIT PRODUCTS IN KBr DISCS (FREQUENCIES ARE IN cm^{-1})

Compound	ν_{C-H} R	ν_{C-H} Ar	ν_{N-O}	ν_{Et-Cl}(ter)	Other Vibrations
$Pt_2(Meaao)_2Cl_2$	2920(w)	3060(w)	1290(vs)	—	1580(w),1430(m),1450(m),1430(s), 1385(s),1350(s),1325(s),1150(w), 1070(m),1000(m),900(m),760(s), 720(s),680(s),615(s),600(m),590(m), 580(m),510(m).
$[(Meaao)Pt(NH_2C_6H_5)Cl]$	2920(w)	3040(w)	1260(vs)	350(m)	3250(s),3190(m),1590(m),1570(m), 1485(s),1465(m),1450(m),1435(m), 1380(s),1330(s),1200(w),1160(s), 1025(w),1000(m),905(m),760(s), 750(s),720(m),680(s),630(m),615(m), 560(m),540(m),520(m).
$[(Meaao)Pt(py)Cl]$	2920(w)	3060(w)	1270(vs)	340(m)	1610(s),1480(s),1450(s),1435(m), 1390(s),1340(s),1220(m),1150(m), 1070(m),1050(m),1000(m),900(m), 755(s),730(s),680(s),635(m), 620(m),520(m).

w = weak; m = medium; s = strong; vs = very strong.

its palladium analogue i.e. structure II.
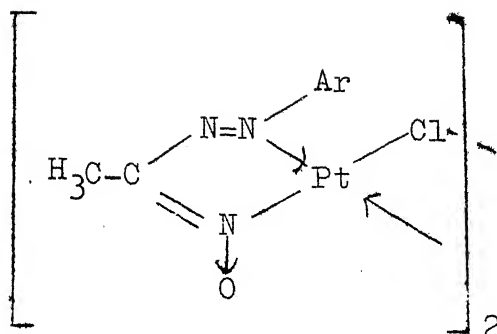
II

B. Bridge-splitting Reactions of $Pt_2(Meaao)_2Cl_2$

$Pt_2(Meaao)_2Cl_2$ undergoes facile bridge-splitting reactions
with Lewis bases like py and aniline eg.

$$Pt_2(Meaao)_2Cl_2 + 2B \xrightarrow{\ bz\ } 2 \left[(Meaao)Pt(B)Cl\right] \qquad \ldots.(2)$$
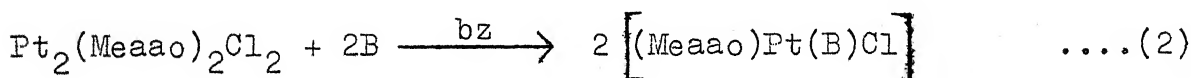
$$B = py, \text{ aniline}$$

III

When stoichiometric amount of the base is added to the
solution of $Pt_2(Meaao)_2Cl_2$ in benzene and the resulting purple
solution is concentrated to small volume, the bridge-split
product III separates out as violet crystalline solid.

The spectral characteristics of the bridge-split products
are very much similar to those of the corresponding palladium
analogues. In the infrared spectrum of $\left[(Meaao)Pt(NH_2C_6H_5)Cl\right]$,

ν_{N-H} appears at 3250 and 3190 cm^{-1} and δ_{NH_2} is observed at 1570 cm^{-1} (Fig. VI.1). The characteristic vibrations of coordinated pyridine are all present in the infrared spectrum of $\left[(Meaao)Pt(py)Cl\right]$. The vibration frequencies of $\left[(Meaao)Pt(NH_2C_6H_5)Cl\right]$ and $\left[(Meaao)Pt(py)Cl\right]$ are set out in Table VI.1. In benzene, both the complexes exhibit an intense band at 565 nm with ϵ = 5000 and 4900 respectively. The band positions for the corresponding palladium complexes are at 515 nm and 520 nm. The red shift of the band in case of platinum complexes is again suggestive of M $\longrightarrow$ L charge transfer assignment.

C. Bis(phenylazoacetaldoximato)palladium(II): Synthesis and Structure

The addition of an ethanolic solution of two mols of phenylazoacetaldoxime to an aqueous solution of K_2PtCl_4 (one mol) does not bring about any immediate reaction. However, on prolonged stirring (48 hrs), a dark solid separates out from the reaction mixture. Part of this solid is soluble in ethanol and is removed while washing the dark solid with ethanol. The rest part dissolves in chloroform to give a greenish brown solution. Addition of ethanol to this solution deposits dark shinning crystals of composition $Pt(Meaao)_2$.

$$K_2PtCl_4 + 2\ HMeaao \xrightarrow{aq.\ EtOH} Pt(Meaao)_2 + 2KCl + 2HCl \quad \ldots(3)$$
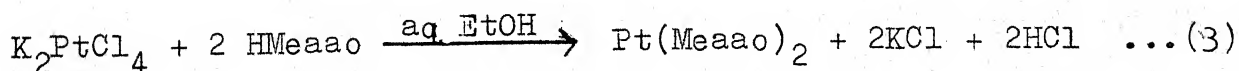
The infrared spectrum of $Pt(Meaao)_2$ is however, entirely different from that of $Pd(Meaao)_2$. The spectrum is displayed

in Fig. VI.2 and the vibration frequencies are listed below.

3060(w), 2920(w), 1475(m), 1450(s), 1370(w), 1330(m), 1300(m), 1240(vs), 1170(s), 1145(s), 1070(w), 975(s), 830(m), 760(s), 710(m), 690(m), 630(m), 620(m), 560(s).

This anomaly is quite surprising since the reactions of $Pt(Meaao)_2$ are found to be similar to those of $Pd(Meaao)_2$ (vide infra).

The electronic spectrum of $Pt(Meaao)_2$ in benzene exhibits an intense band at 1050 nm (ϵ =6400) with a shoulder at 970 nm (ϵ =6000). The appearance of such intense band at low energy region is rather unusual. Nevertheless it is significant to note that the double-humped structure and intensity of the band at 1050 nm are very much similar to those of the $\sim$ 600 nm band of $Pd(Meaao)_2$ (Fig. VI.3). Moreover, the red shift of the band in case of $Pt(Meaao)_2$ indicates that it might originate from a metal $\longrightarrow$ ligand (M $\longrightarrow$ L) charge transfer.

The most unusual observation with $Pt(Meaao)_2$ is that the complex gives rise to very broad, almost nondetectable nmr signals for both Me and Ph groups. When this was observed for the first time, it was suspected that the signals could not be detected because of excessive broadening due to some paramagnetic species. The compound was then subjected to epr studies and it was indeed found that it gives rise to well-defined epr signal both in solid state ($g_{\perp}$ = 1.961; $g_{\parallel}$ = 1.936) and in
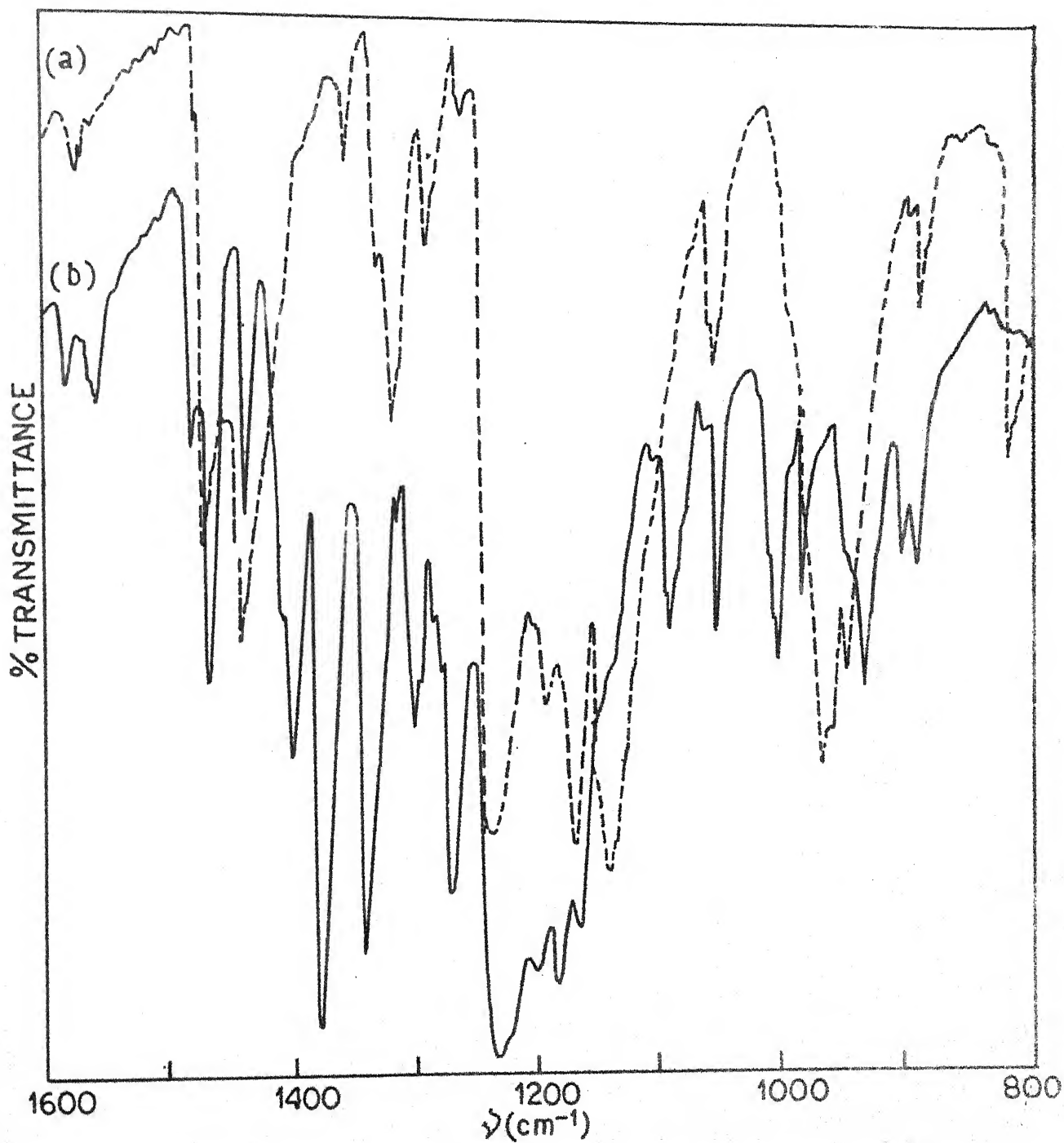
FIG. Ⅵ. 2. PARTIAL INFRARED SPECTRA OF (a) Pt (Meaao)₂
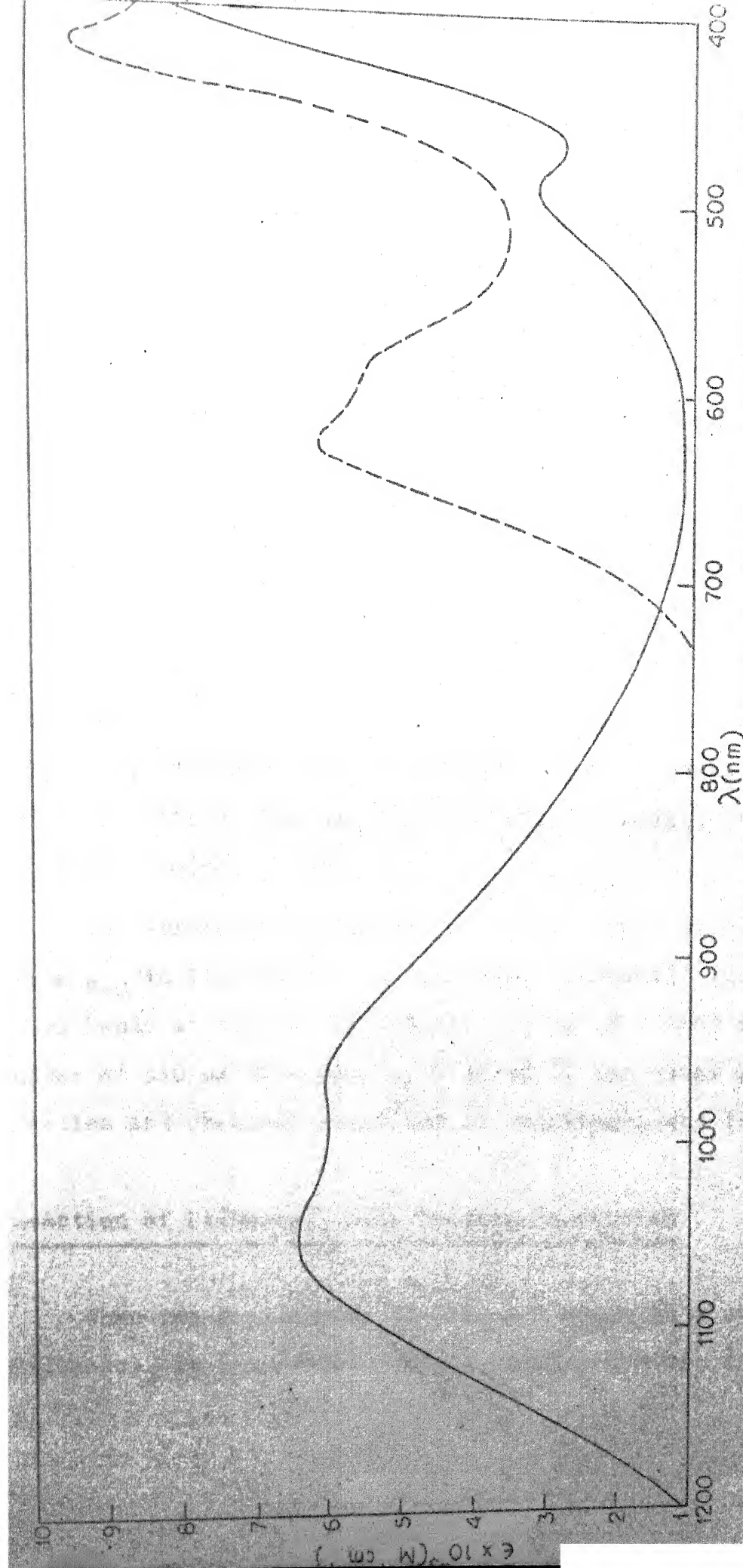AND (b) Pt (Phaao)₂ IN KBr (DISC).

FIG. XI. 3 ELECTRONIC SPECTRUM OF BIS(PHENYLAZOACETALDOXIMATO) PLATINUM(II) IN BENZENE (————). THE ELECTRONIC SPECTRUM OF THE CORRESPONDING PALLADIUM(II) COMPLEX IN BENZENE (————) IS SHOWN FOR THE SAKE OF COMPARISON.

chloroform solution (g = 1.965). However, the bulk magnetic susceptibility measurement on solid Pt(Meaao)$_2$ shows it to be completely diamagnetic. The observed epr signal apparently arises from a paramagnetic species present in small concentration. The nature of this species and its relationship to the Pt(Meaao)$_2$ composition is under investigation.

Pt(Phaao)$_2$ has also been synthesised following similar procedure. The infrared spectrum of Pt(Phaao)$_2$ closely resembles that of Pd(Phaao)$_2$. The vibration frequencies are set out below.

3060(w), 1590(w), 1570(w), 1480(m), 1455(m), 1410(m), 1390(s), 1355(s), 1315(m), 1280(m), 1240(vs), 1210(s), 1195(s), 1110(m), 1075(m), 1025(m), 950(m), 915(m), 780(m), 765(s), 740(s), 730(m), 690(s), 660(m), 625(m), 610(s), 560(m), 510(w).

The strong absorption at 1240 cm^{-1} (Fig. VI.2) appears to be ν_{N-O} in Pt(Phaao)$_2$. In benzene, Pt(Phaao)$_2$ exhibits intense bands at 1085 nm (ϵ =3500), 790 nm (ϵ =2600) and a shoulder at 510 nm (ϵ = 2500). Studies on the other spectral properties and chemical reactions of Pt(Phaao)$_2$ are in progress.

D. Reaction of Pt(Meaao)$_2$ with Triphenylphosphine

When two equivalents of PPh$_3$ are added to a suspension of Pt(Meaao)$_2$ in dehydrated ethanol and the mixture is stirred

for 6 hrs, a clear red solution is obtained from which
$\left[(Meaao)_2Pt(PPh_3)_2\right]$ separates out as orange crystalline solid
e.g.

$$Pt(Meaao)_2 + 2PPh_3 \xrightarrow[\text{stir}]{\text{EtOH}} \quad \text{IV structure} \qquad \ldots(4)$$
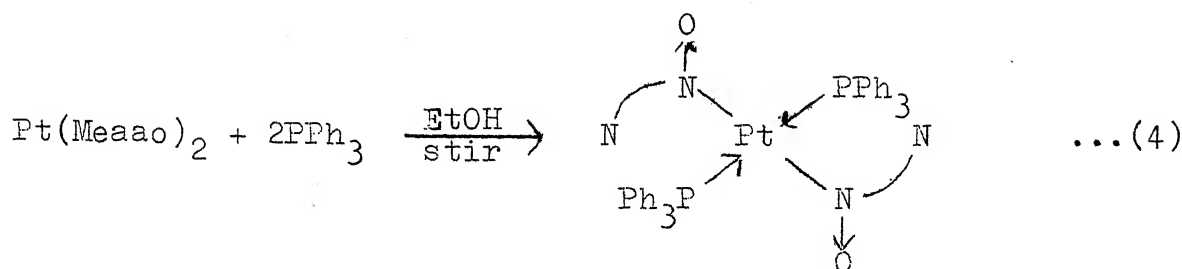
IV

The infrared spectrum of $\left[(Meaao)_2Pt(PPh_3)_2\right]$ shows
that both the aao fragments are in open-azo configuration
(Table VI.2). Since the spectrum (Fig.4) is very much similar
to that of $\left[(Meaao)_2Pd(PPh_3)_2\right]$, it is believed that in solid
state the complex has the structure **IV**. However, $\left[(Meaao)_2Pt(PPh_3)_2\right]$
dissolves in benzene and chloroform to produce orange-red
solutions. The room temperature pmr spectrum of $\left[(Meaao)_2Pt(PPh_3)_2\right]$
exhibits a broad methyl signal at $\delta = 1.73$ ppm. Most possibly
the complex loses one molecule of PPh_3 in solution and the
methyl signal of the resulting species namely $\left[(Meaao)_2Pt(PPh_3)\right]$
is broadened due to fast exchange between open and closed aao
chelate ring. Similar observation has been made with
$\left[(Meaao)_2Pd(PPh_3)_2\right]$ (Chapter V).

E. Reaction of $Pt(Meaao)_2$ with 1,2-bis(diphenylphosphino)ethane
_____

In dehydrated ethanol, $Pt(Meaao)_2$ reacts slowly with
diphos (molar ratio 1:1) to produce the complex $\left[(Meaao)_2Pt(diphos)\right]$

INFRARED DATA (IN KBr DISCS) OF PLATINUM(II) COMPLEXES WITH BOTH
ARYLAZOOXIMATO CHELATE RINGS OPEN (FREQUENCIES ARE IN cm^{-1})

Compound	ν_{C-H} R	Ar	ν_{N-O}	Other Vibrations
[(Meaao)$_2$Pt(PPh$_3$)$_2$]	2920(w)	3060(m)	1240(vs)	1580(w),1490(m),1480(s),1430(s),1380(w), 1340(s),1300(m),1280(w),1185(m),1090(s), 1010(m),1000(m),925(m),770(m),745(s), 710(s),690(s),620(m),600(s),570(s), 525(s),520(s),500(m).
[(Meaao)$_2$Pt(diphos)]	2920(w)	3040(m)	1240(vs)	1580(w),1570(w),1490(m),1480(s),1430(s), 1400(w),1340(s),1310(m),1290(w),1150(w), 1100(s),1065(w),1000(s),820(m),760(m), 740(m),715(m),705(s),685(s),580(m), 550(m),525(s),480(s).

w = weak; m = medium; s = strong; vs = very strong.
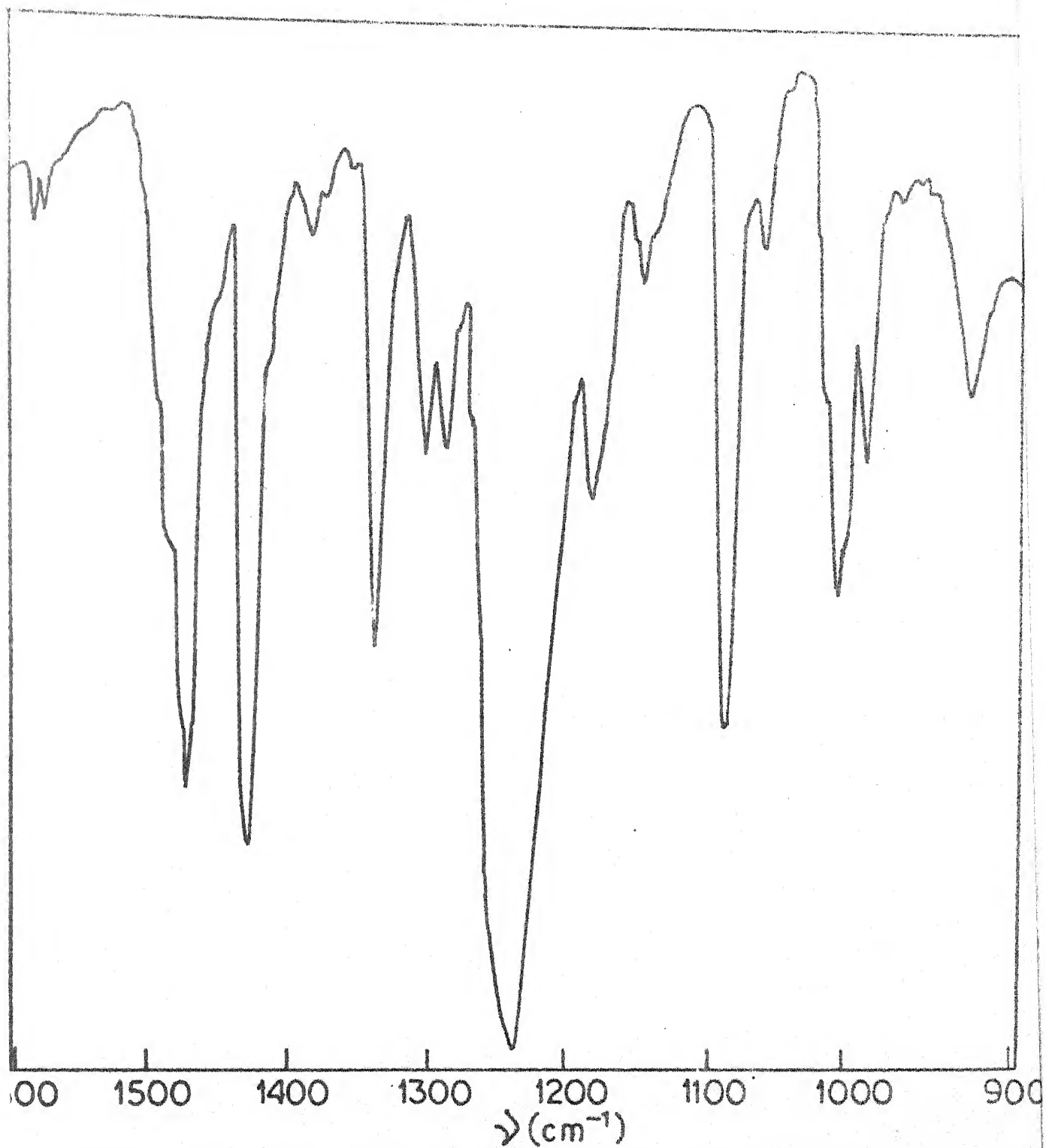
FIG VI.4. PARTIAL INFRARED SPECTRUM OF $[(Meaao)_2 Pt(PPh...$

IN KBr(DISC).

(reaction(5)). The infrared spectrum of the complex in KBr (Table VI.2) demonstrates that both the aao fragments are open

$$Pt(Meaao)_2 + Ph_2PCH_2CH_2PPh_2 \longrightarrow \qquad \qquad \qquad \qquad ...(5)$$

V
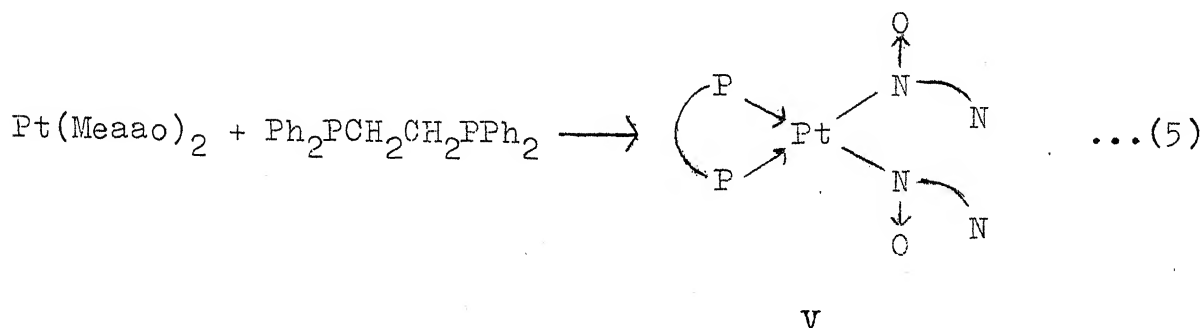
at the azo-end (structure V). Since the electronic spectrum of $\left[(Meaao)_2Pt(diphos)\right]$ in chloroform (or benzene) exhibits no band around 500 nm, it is evident that the aao fragments remain in the open-azo configuration even in solution. In the room temperature pmr spectrum of $\left[(Meaao)_2Pt(diphos)\right]$ in $CDCl_3$ (Fig. VI.5), one sharp methyl signal with ^{195}Pt satellites ($^4J_{Pt-H} = 5$ Hz) is observed at $\delta = 1.77$ ppm. Similar high-field shift of the methyl signal due to anisotropic diamagnetic shielding by the phenyl groups of diphos has been observed with $\left[(Meaao)_2Pd(diphos)\right]$ and $\left[(Meaao)Pd(diphos)Cl\right]$.

F. Oxidative Addition of Phenylazoacetaldoxime to $\left[Pt(PPh_3)_4\right]$

The oxidative addition of two mols of phenylazoacetald-oxime to one mol of tetrakis(triphenylphosphine)platinum(0) leads to the formation of $\left[(Meaao)_2Pt(PPh_3)_2\right]$. On stirring (under nitrogen) a suspension of $\left[Pt(PPh_3)_4\right]$ with two equivalents of HMeaao in dehydrated ethanol, a violet solution is obtained
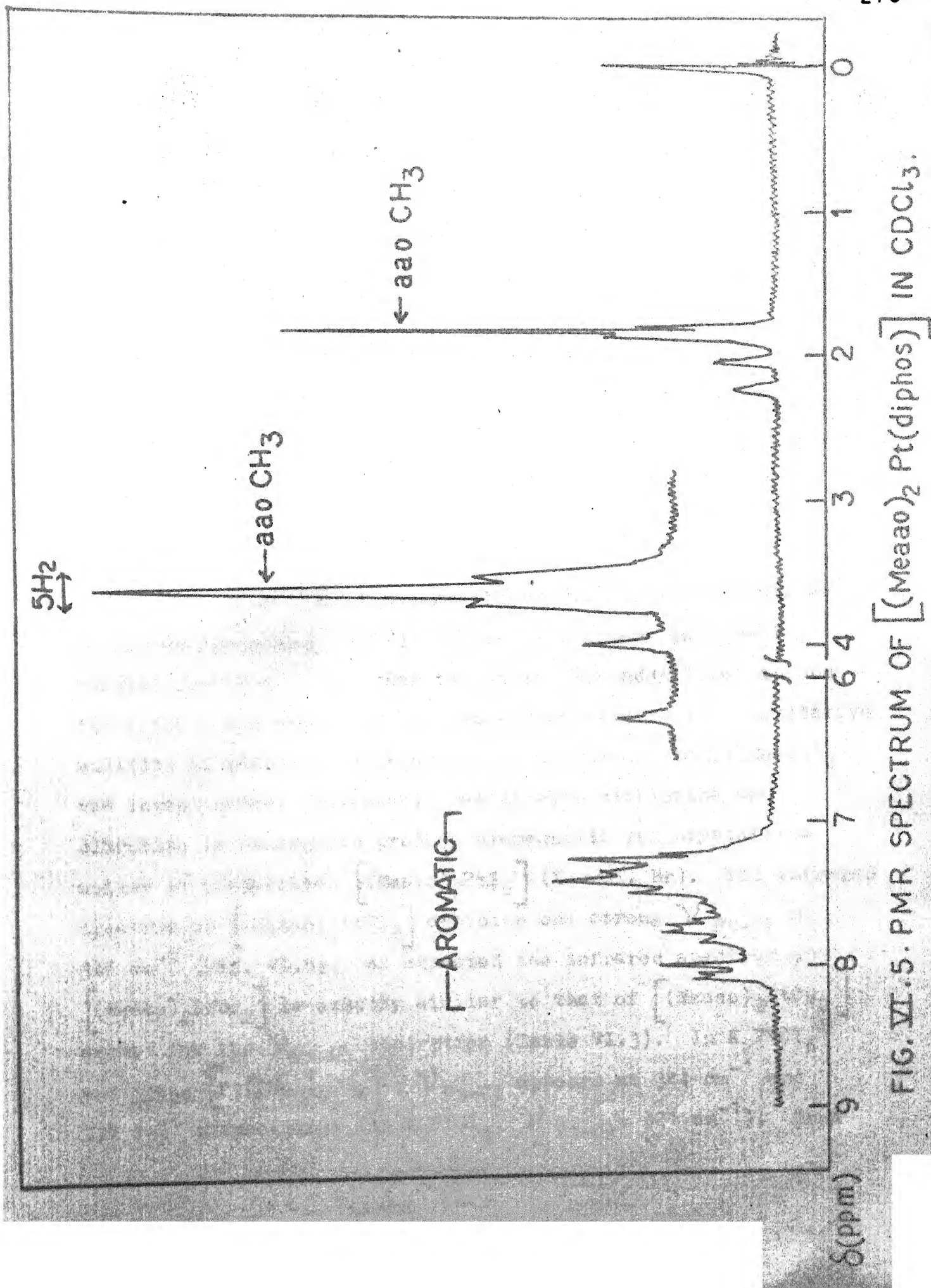
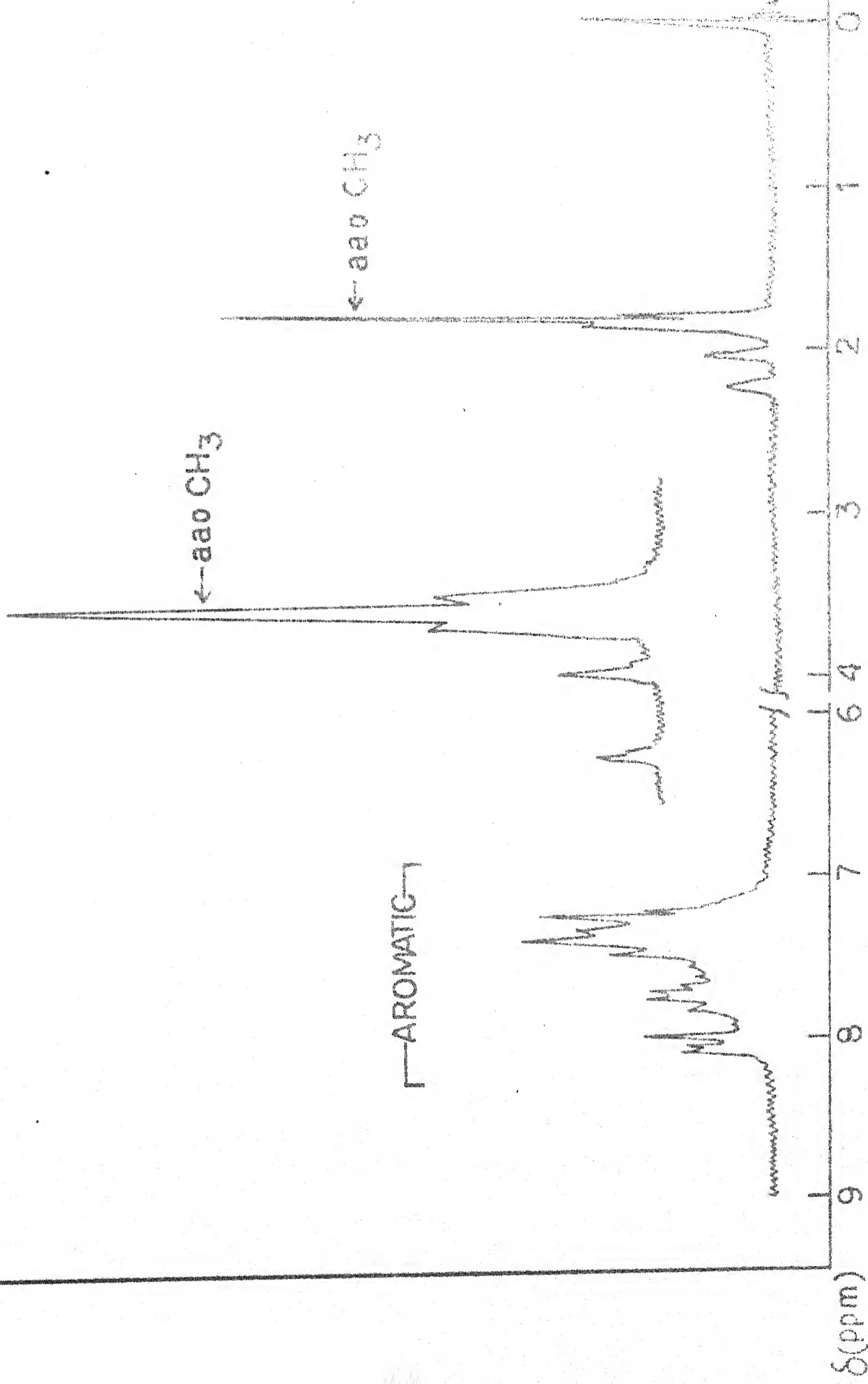FIG. VI.5. PMR SPECTRUM OF $\left[(\text{Meaao})_2 \text{Pt}(\text{diphos})\right]$ IN CDCl$_3$.

FIG. VI.5. PMR SPECTRUM OF $[(Meaao)_2 Pt(diphos)]$ IN $CDCl_3$.

from which orange crystals of $\left[(\text{Meaao})_2\text{Pt}(\text{PPh}_3)_2\right]$ separate out within 6 hrs.

When $\left[\text{Pt}(\text{PPh}_3)_4\right]$ is stirred (under nitrogen) with two equivalents of phenylazobenzaldoxime in dehydrated ethanol, the product is a dark crystalline solid which does not contain triphenylphosphine in it. The infrared spectrum of the dark solid is somewhat similar to that of $\text{Pt}(\text{Phaao})_2$. The nature of this compound is yet to be characterised.

G. Oxidative Addition of Halogens to Pt(Meaao)$_2$

The oxidation of square-planar platinum(II) complexes to the corresponding Pt(IV) species by halogens is a well studied reaction[1]. In order to gather some additional informations about the nature of the bis-arylazooximes, the oxidative addition of halogens (dichlorine and dibromine) to $\text{Pt}(\text{Meaao})_2$ was investigated. $\text{Pt}(\text{Meaao})_2$ reacts with dichlorine and dibromine in benzene to produce diamagnetic red crystalline solids of composition $\left[(\text{Meaao})_2\text{PtX}_2\right]$ (X = Cl, Br). The infrared spectrum of $\left[(\text{Meaao})_2\text{PtCl}_2\right]$ exhibits one strong $\nu_{\text{Pt-Cl}}$ at 345 cm^{-1} (Fig. VI.6). As expected the infrared spectrum of $\left[(\text{Meaao})_2\text{PtBr}_2\right]$ is exactly similar to that of $\left[(\text{Meaao})_2\text{PtCl}_2\right]$ except for the $\nu_{\text{Pt-Cl}}$ absorption (Table VI.3). In K_2PtCl_6[2] and $\underline{\text{trans}}$-$\left[\text{Pt}(\text{PMe}_3)_2\text{Cl}_4\right]$[3], $\nu_{\text{Pt-Cl}}$ appears at 344 cm^{-1} and 337 cm^{-1} respectively (in K_2PtCl_4, $\nu_{\text{Pt-Cl}} = 321$ cm^{-1}). Thus
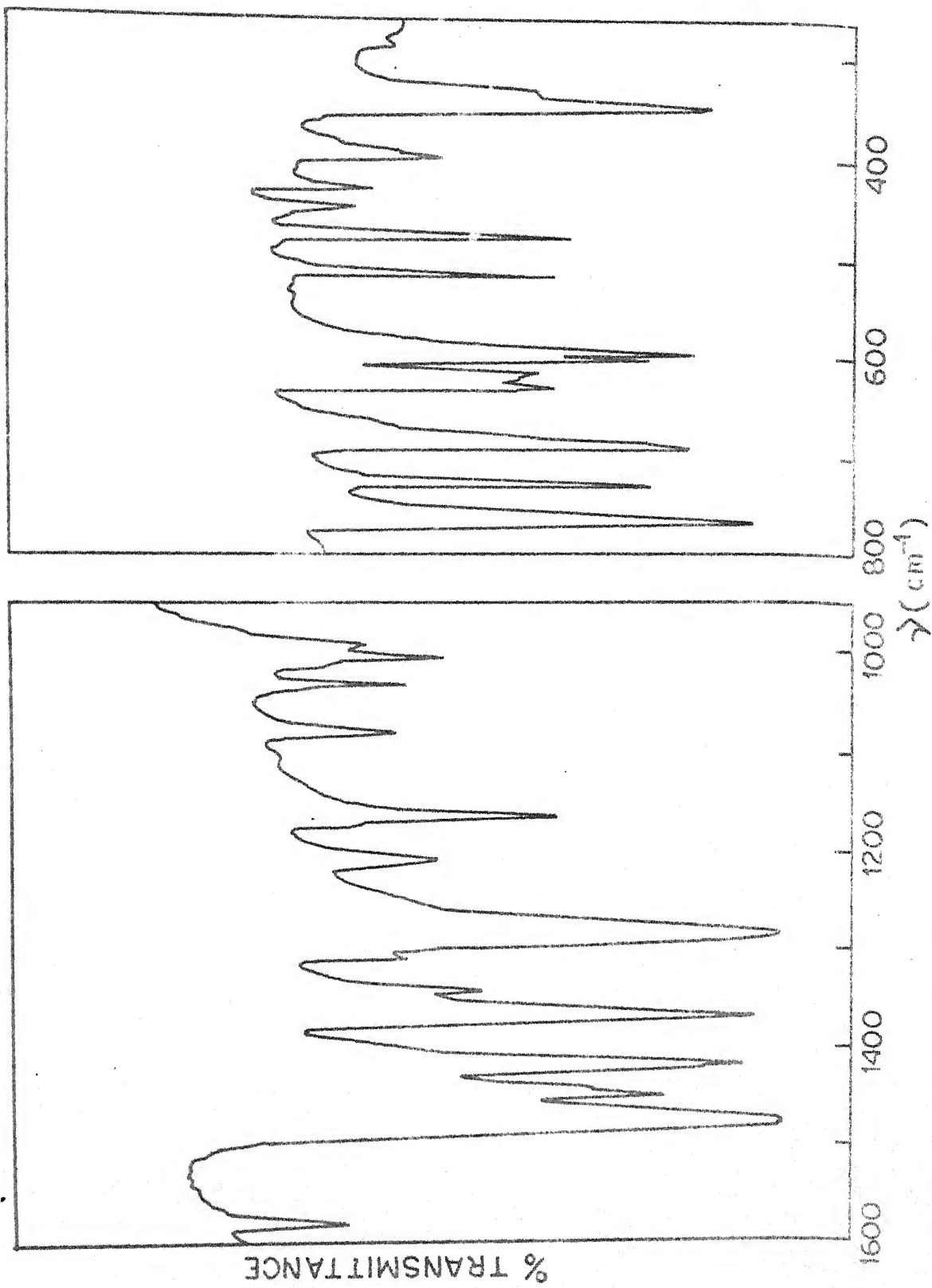
FIG VI.6. PARTIAL INFRARED SPECTRUM OF $[(Meaao)_2 PtCl_2]$ IN KBr (DISC).

TABLE 4.3

INFRARED DATA OF $\left[(Meaao)_2 Pd^{IV} X_2\right]$ (X = Cl, Br) COMPLEXES
IN KBr DISCS (FREQUENCIES ARE IN cm^{-1}).

Compound	ν_{C-H}		ν_{N-O}	ν_{Pt-Cl}	Other Vibrations
	R	Ar			
$\left[(Meaao)_2 PtCl_2\right]$	2920(w)	3060(w)	1290(vs)	345(s)	1580(m),1480(s),1450(s),1420(s), 1370(s),1210(w),1160(s),1100(w), 1070(w),1020(m),1000(m),870(m), 830(m),760(s),720(s),685(s), 625(m),610(m),600(s),520(m), 480(m),400(m).
$\left[(Meaao)_2 PtBr_2\right]$	2920(w)	3060(w)	1285(vs)	–	1580(m),1470(s),1450(s),1420(s), 1370(s),1210(w),1170(m),1160(m), 1070(w),1025(m),1000(m),870(m), 820(m),760(s),720(s),685(s), 625(m),620(m),590(m),510(m), 470(m).

w = weak; m = medium; s = strong; vs = very strong.

the Pt-Cl stretching vibration and the observed diamagnetism collectively suggest that both $\left[(\text{Meaao})_2\text{PtCl}_2\right]$ and $\left[(\text{Meaao})_2\text{PtBr}_2\right]$ are Pt(IV) complexes. Since only one $\nu_{\text{Pt-Cl}}$ is observed, $\left[(\text{Meaao})_2\text{PtCl}_2\right]$ (and the bromo-species) is expected to have a trans- configuration (structure VI.
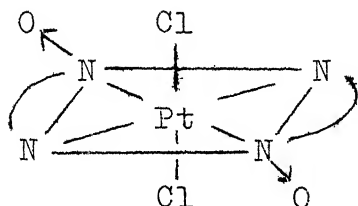

VI

$\left[(\text{Meaao})_2\text{PtCl}_2\right]$ dissolves in benzene, chloroform and acetone to give deep red solutions which are quite stable. In benzene, the complex exhibits a band at 530 nm ($\epsilon = 6000$) with a shoulder at 460 nm ($\epsilon = 4900$). $\left[(\text{Meaao})_2\text{PtBr}_2\right]$ however, decomposes slowly in solution to produce a brown precipitate.

The methyl signal in the room temperature pmr spectrum of $\left[(\text{Meaao})_2\text{PtCl}_2\right]$ appears at $\delta = 2.4$ ppm (Fig. VI.7). In case of $\left[(\text{Meaao})_2\text{PtBr}_2\right]$, a strong methyl signal is observed at $\delta = 2.56$ ppm together with a weak one at $\delta = 2.38$ ppm. This weak signal slowly gains intensity with time and at the same time a sharp signal at $\delta = 7.6$ ppm starts appearing. Most possibly these signals arise from the decomposition products of $\left[(\text{Meaao})_2\text{PtBr}_2\right]$ in solution. The decomposition products could not be identified so far.

FIG. VI. 7. NMR SPECTRUM OF [(Meaao)$_2$ Pt Cl$_2$] IN CDCl$_3$.

←aao CH$_3$

⌐AROMATIC⌐

δ(ppm)
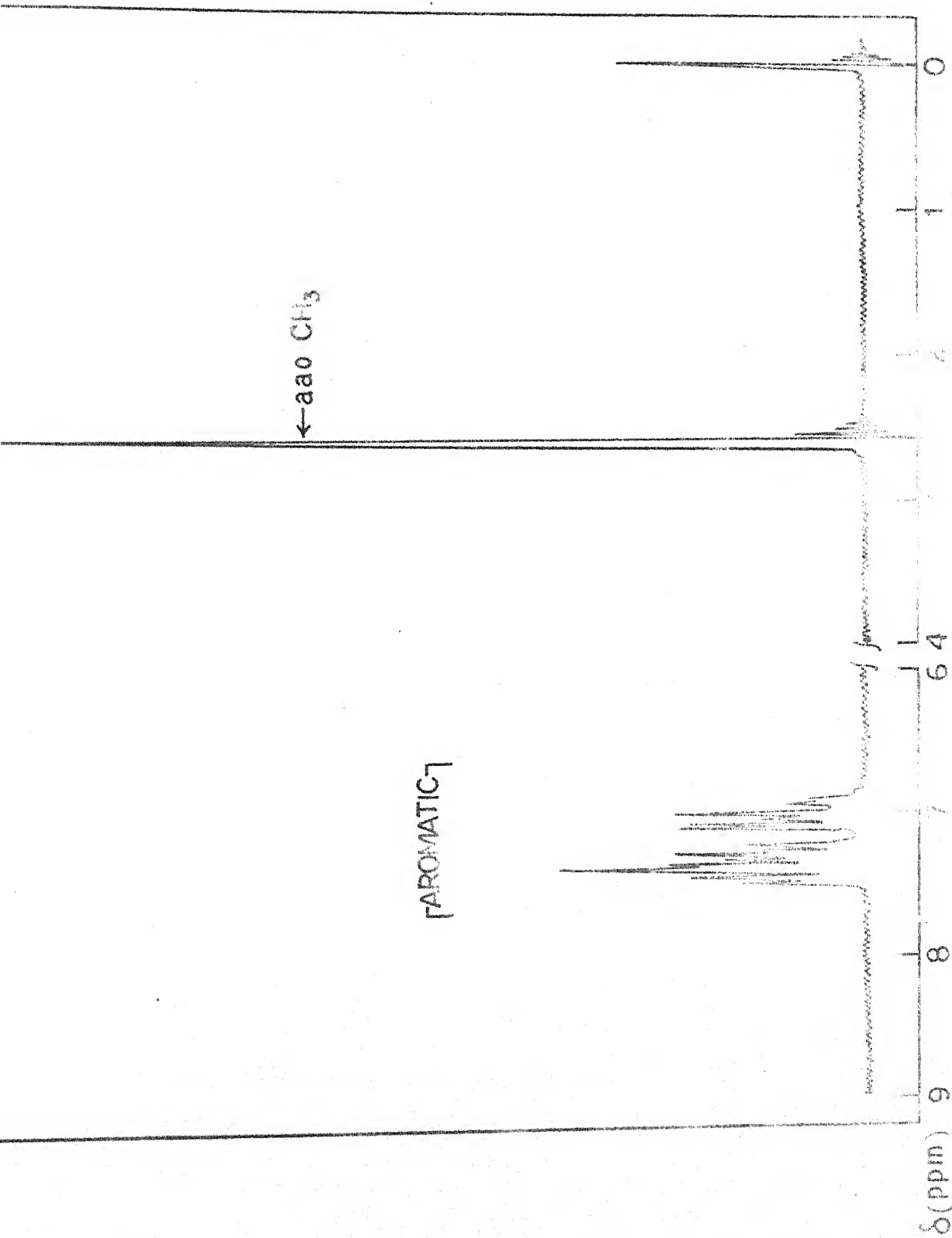
H. Reaction of HCl with $\left[(Meaao)_2Pt(PPh_3)_2\right]$

The binding of the aao fragment through the oxime-end to Pt atom in $\left[(Meaao)_2Pt(PPh_3)_2\right]$ is clearly demonstrated by the reaction of the complex with HCl which is known to open the oxime-end of the aao chelate ring. When HCl gas is passed through a solution of $\left[(Meaao)_2Pt(PPh_3)_2\right]$ in benzene, the initial red color turns light yellow and slowly pale yellow crystals of trans-$\left[(PPh_3)_2PtCl_2\right]$ separate out. Assuming that no rearrangement has taken place in course of the reaction, the formation of trans-$\left[(PPh_3)_2PtCl_2\right]$ suggests a trans- disposition of the two PPh$_3$ molecules in $\left[(Meaao)_2Pt(PPh_3)_2\right]$ (structure IV). Trans-$\left[(PPh_3)_2PtCl_2\right]$ has been synthesised by irradiating cis-$\left[(PPh_3)_2PtCl_2\right]$ at 366nm [4]. The reaction sequence (6) is

$$Pt(Meaao)_2 \xrightarrow[bz]{2PPh_3} \left[(Meaao)_2Pt(PPh_3)_2\right] \xrightarrow{HCl} trans-\left[(PPh_3)_2PtCl_2\right] \quad ...(6)$$
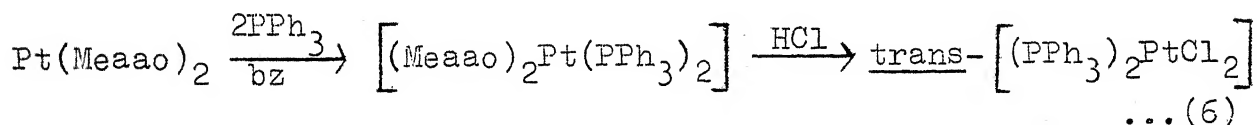
important since it provides a method for obtaining the trans-isomer without recourse to photolysis..

I. Reaction of HCl with Pt(Meaao)$_2$

Introduction of dry HCl gas to the solution of Pt(Meaao)$_2$ in benzene brings about a sharp color change from green to red. When the red solution is poured into water and stirred, the bis-complex is regenerated. Addition of hexane

to the red solution deposits a deep red solid which exhibits broad ν_{O-H} at $\sim$ 3100 cm^{-1} and $\nu_{Pt-Cl(terminal)}$ at 350 cm^{-1} in the infrared spectrum. Since addition of PPh$_3$ to the red solution produces pale yellow crystals of <u>trans</u>-$\left[(PPh_3)_2PtCl_2\right]$, it appears that the species in solution possibly contains aao fragments bound to Pt atom through the azo-end only. However, attempts to convert the red solid to Pt$_2$(Meaao)$_2$Cl$_2$ by treatment with mild bases (including water) failed. Thus the nature of the species present in the red solution is yet not clear.

J. <u>Concluding Remarks</u>

The results obtained so far are sufficient to point out that the Pt-Raao chemistry is not exactly parallel to the Pd-Raao chemistry. The synthesis of halo-bridged arylazooximates of platinum(II) has been possible by only one method and the yield is very low. It appears that the halo-bridged species need more drastic synthetic conditions. However, the spectral properties and reactions of the halo-bridged arylazooximates of platinum(II) are found to be similar to those of the corresponding palladium(II) species. On the other hand, the procedures for the synthesis of bis-arylazooximates of platinum(II) are well established but the complexes possess some unusual spectral characteristics. Nevertheless the reactions of the bis-complexes of platinum(II) are similar to those of the palladium(II) analogues. Thorough studies on the chemistry of the arylazo-oximates of platinum are in progress in this laboratory.

VI.3 EXPERIMENTAL SECTION

A. Preparation of Compounds

a. Chemicals

Potassium tetrachloroplatinate(II) and platinum(II) chloride were procured from Johnson Matthey Chemicals Ltd (London) and Strem Chemicals Inc.(U.S.A.) respectively.

b. The Complexes

(i) Di-μ-chlorobis[phenylazoacetaldoximatoplatinum(II)]

106 mg (0.4 mmol) of platinum(II) chloride and 65 mg (0.4 mmol) of phenylazoacetaldoxime were taken in 20 ml of dehydrated ethanol and the mixture was boiled to reflux for 10 hrs when a dark violet solution was obtained. It was then filtered and the filtrate was allowed to evaporate slowly in vacuum. After 24 hrs, the violet needle-shaped crystals which separated were collected by filtration, washed with ethanol and dried over fused $CaCl_2$ (yield $\sim$ 20%).

(ii) The [(Meaao)Pt(am)Cl] Complexes where am = py and aniline

Both the complexes were prepared in an analogous manner. The synthesis of [(Meaao)Pt(aniline)Cl] is described below.

To a solution of 40 mg (0.05 mmol) of di-μ-chlorobis
[phenylazoacetaldoximatoplatinum(II)] in 15 ml of benzene was
added 2 drops of freshly distilled aniline. The initial violet
color turned purple. The solution was then completely evaporated
in rotary evaporator. The violet solid thus obtained was finally
recrystallised from benzene (yield ~ 80%).
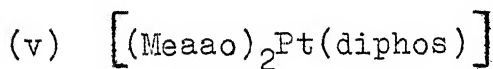
(iii) Bis(phenylazoacetaldoximato)platinum(II)

A solution containing 415 mg (1 mmol) of K_2PtCl_4 in
25 ml of water was mixed with a solution of 326 mg (2 mmol) of
phenylazoacetaldoxime in 20 ml of ethanol and the mixture was
stirred at room temperature for 48 hrs when a dark solid was
obtained. The solid was filtered and washed with ethanol till
the filtrate which was initially violet became colorless. The
residue (dark in color) was dried and then redissolved in
minimum volume of chloroform. 10 ml of ethanol was added to
the greenish brown chloroform solution and the mixture was kept
in air. Dark shinning needles of $Pt(Meaao)_2$ separated within
1 hr. The crystals were collected by filtration, washed with
minimum volume of ethanol and dried over fused $CaCl_2$ (yield ~ 70%).

Bis(phenylazobenzaldoximato)platinum(II) was synthesised
from K_2PtCl_4 and phenylazobenzaldoxime following a similar
procedure.

(iv) $\left[(\text{Meaao})_2\text{Pt}(\text{PPh}_3)_2\right]$
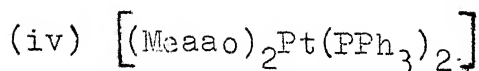
105 mg (0.4 mmol) of triphenylphosphine (in 5 ml of dehydrated ethanol) was added to a suspension of 104 mg (0.2 mmol) of bis(phenylazoacetaldoximato)platinum(II) in 20 ml of dehydrated ethanol and the mixture was stirred for 6 hrs. The initial green color slowly changed to red and after 4 hrs orange crystals of $\left[(\text{Meaao})_2\text{Pd}(\text{PPh}_3)_2\right]$ started separating out. The crystals were filtered, washed with cold dehydrated ethanol and dried in vacuum over fused $CaCl_2$ (yield $\sim$ 80%).

Benzene was also used as the solvent for this synthesis.

(v) $\left[(\text{Meaao})_2\text{Pt}(\text{diphos})\right]$

A suspension of 156 mg (0.3 mmol) of bis(phenylazo-acetaldoximato)platinum(II) in 20 ml of dehydrated ethanol was stirred with 120 mg (0.3 mmol) of 1,2-bis(diphenylphosphino)ethane for 48 hrs. The initial green color turned brown during this period and orange yellow needles of $\left[(\text{Meaao})_2\text{Pt}(\text{diphos})\right]$ were deposited. After 48 hrs, the crystals were collected by filtration, washed with dehydrated ethanol and dried in vacuum over fused $CaCl_2$. The complex was finally recrystallised from chloroform (yield $\sim$ 70%).

(vi) Oxidative Addition of HMeaao to $[Pt(PPh_3)_4]$

Tetrakis(triphenylphosphine)platinum(O), $[Pt(PPh_3)_4]$ was synthesised as described in the literature[5].

To a suspension of 249 mg (0.2 mmol) of $[Pt(PPh_3)_4]$ in 20 ml of dehydrated ethanol stirring under nitrogen was added a solution containing 66 mg (0.4 mmol) of phenylazoacetaldoxime in 10 ml of dehydrated ethanol. A clear red solution was obtained within 1 hr. As the stirring was continued, orange crystals started separating out. After 6 hrs, the crystals were filtered, washed with dehydrated ethanol and finally dried in vacuum over fused $CaCl_2$ (yield $\sim$ 75%).

(vii) The $[(Meaao)_2PtX_2]$ Complexes where X = Cl, Br Oxidation of $Pt(Meaao)_2$ with Dichlorine

About 200 mg of bis(phenylazoacetaldoximato)platinum(II) was dissolved in 20 ml of benzene and a SLOW stream of dichlorine was allowed to pass through this greenish brown solution. As a few bubbles of dichlorine were passed, the color of the solution turned deep red. The passage of dichlorine was then stopped and the red solution was slowly concentrated (on hot plate) to $\sim$ 2 ml. The sides of the beaker were scratched when violet crystals of $[(Meaao)_2PtCl_2]$ separated. The crystals were filtered, washed with hexane and dried in vacuum (yield $\sim$ 70%).

Oxidation of Pt(Meaao)$_2$ with Dibromine

To a solution containing 260 mg (0.5 mmol) of bis(phenylazoacetaldoximato)platinum(II) in 20 ml of benzene was added with stirring a solution of 80 mg (0.5 mmol) of dibromine in 2 ml of benzene. The initial greenish brown color changed to deep red. The red solution was then concentrated (on hot plate) to $\sim$ 2 ml and to it 5 ml of hexane was added when violet crystals of $\left[(\text{Meaao})_2\text{PtBr}_2\right]$ were deposited. The crystals were collected by filtration, washed with hexane and finally dried in vacuum (yield $\sim$ 70%).

(viii) Reaction of HCl with $\left[(\text{Meaao})_2\text{Pt}(\text{PPh}_3)_2\right]$

A slow stream of HCl gas was allowed to pass through a solution containing 104 mg (0.1 mmol) of $\left[(\text{Meaao})_2\text{Pt}(\text{PPh}_3)_2\right]$ in 10 ml of benzene. As a few bubbles of HCl were passed through the solution, the initial red color turned light yellow. Addition of ethanol ($\sim$ 5ml) to this yellow solution deposited pale yellow crystals of trans-$\left[(\text{PPh}_3)_2\text{PtCl}_2\right]$ (yield $\sim$ 80%).

B. Characterisation of Complexes

This was done by C, H, N microanalysis. Characterisation data for the complexes are collected in Table VI.4.

CHARACTERISATION DATA OF PLATINUM COMPLEXES

Compound	MP°C[a]	% C		% H		% N	
		Calc.	Found	Calc.	Found	Calc.	Found
$Pt_2(Meaao)_2Cl_2$	154	24.45	24.38	2.05	2.12	10.69	10.71
$[(Meaao)Pt(py)Cl]$	187	33.07	33.10	2.77	2.68	11.87	11.82
$[(Meaao)Pt(NH_2C_6H_5)Cl]$	181	34.58	34.47	3.11	3.21	11.53	11.47
$Pt(Meaao)_2$	188	36.98	37.12	3.10	3.08	16.18	16.10
$Pt(Phaao)_2$	218	48.49	48.41	3.13	3.11	13.05	12.97
$[(Meaao)_2Pt(PPh_3)_2]$	159[b]	59.81	59.90	4.44	4.37	8.05	8.10
$[(Meaao)_2Pt(diphos)]$[c]	–	54.94	55.12	4.39	4.31	9.15	9.20
$[(Meaao)_2PtCl_2]$	>280	32.53	32.70	2.73	2.81	14.23	14.10
$[(Meaao)_2PtBr_2]$	>280	28.28	28.17	2.37	2.32	12.37	12.29

a All melting points reported in this table are uncorrected.

b The complex melts with decomposition.

c The complex changes color (yellow to red) around 155°C and then slowly decomposes
   to a black mass.

C. Physical Measurements

a. Infrared Spectra

Details are given in Chapter II.

b. Electronic Spectra

Details are given in Chapter II.

c. Proton Magnetic Resonance Spectra

Details are given in Chapter II.

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SUMMARY

As the title indicates, this thesis concerns the
chemistry of the arylazooximes of palladium and platinum.
Arylazooximes, R-C(=NOH)-N=N-Ar have a fascinating coordination
chemistry a considerable part of which has been developed in
course of previous investigations in this laboratory. The
present work adds interesting new chapters to the chemistry of
this versetile ligand system.

In the introductory chapter (Chapter I) some aspects of
the known chemistry of palladium in the oxidation states
0, +1, +2 and +4 are briefly reviewed. The purpose of the
present research namely development of the chemistry of the
arylazooximes of palladium and platinum is set in this
background. The ligand system and its abbreviation are shown
in 1 and 2 respectively.

$$R-C \overset{\displaystyle N=N \diagup Ar}{\underset{\displaystyle N}{\diagdown}} \quad OH$$
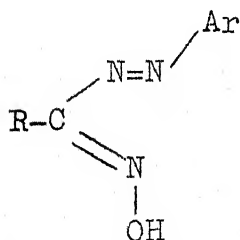
HRaao

R = Me, Ph, p-tol
Ar = Ph

1   2

Chapter II deals with the various synthetic methods and salient structural features of the two types of palladium(II) complexes namely the halo-bridged arylazooximates $Pd_2(Raao)_2X_2$ (3) and the halogen-free bis-arylazooximates $Pd(Raao)_2$ (4).

$$\underline{3} \qquad\qquad\qquad \underline{4}$$
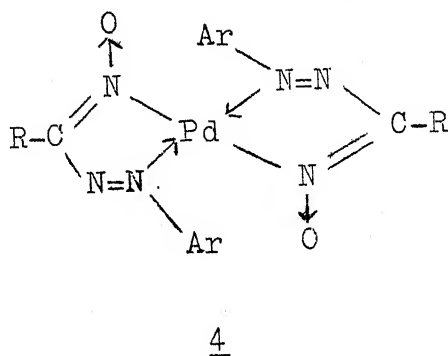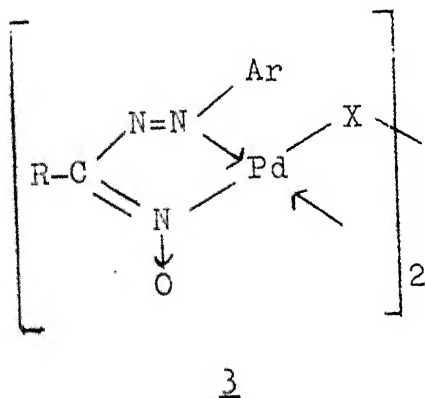
The halo-bridged complexes are formed in

(i)   the 1:1 reaction between K_2PdX_4 and HRaao in aqueous ethanol;

(ii)   the 1:1 reaction between $Pd(PhCN)_2X_2$ and HRaao;

(iii)   the 1:1 reaction between PdX_2 and HRaao in boiling ethanol

and (iv) the reaction between $Pd(Raao)_2$ and halogens (dichlorine and dibromine).

The bis-complexes are formed in

(i)   the 1:2 reaction between K_2PdX_4 and HRaao (R = aryl in aqueous ethanol (in case of HMeaao, Pd: ligand ratio needed for the formation of $Pd(Meaao)_2$ is 1:4);

(ii) the 1:2 reaction between $Pd(PhCN)_2X_2$ and HRaao in
    ethanol

and (iii) the 1:2 reaction between $Pd(sal)_2$ and HRaao in
    benzene.

    In the syntheses of the bis-complexes, the halo-bridged species are formed at the initial step. Further addition of HRaao brings about the bridge-cleavage (by the oxime-end of HRaao) followed by ring closure yielding the bis-arylazooximate as the final product. The presence of water (or Na_2CO_3) is a necessary condition for the formation of bis-complexes since it facilitates the protonation of the oxime group of HRaao.

    The halo-bridged complexes $Pd_2(Raao)_2X_2$ can be converted to the bis-complexes $Pd(Raao)_2$ by the following two routes:

(a) $Pd_2(Raao)_2X_2$ + 2HRaao $\xrightarrow[\text{room temp.}]{\substack{\text{benzene or}\\ \text{chloroform}}}$ red-brown solution

$$\downarrow \text{poured into water}$$

$$Pd(Raao)_2$$

(b) $Pd_2(Raao)_2X_2$ + 2HRaao $\xrightarrow{\substack{\text{benzene or}\\ \text{chloroform}}}$ red-brown solution

$$\downarrow \text{heat with } Na_2CO_3$$
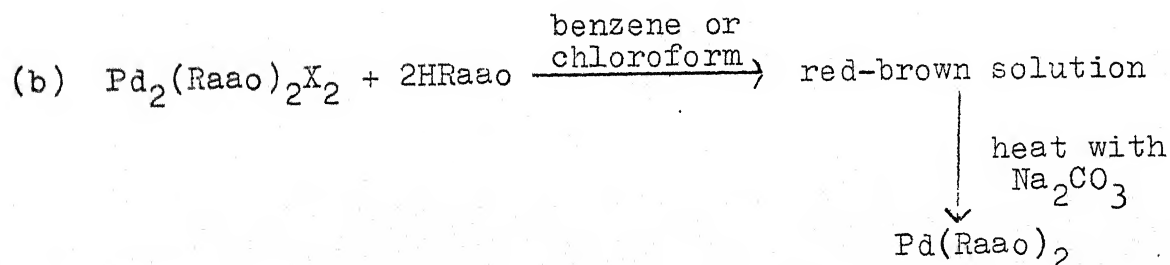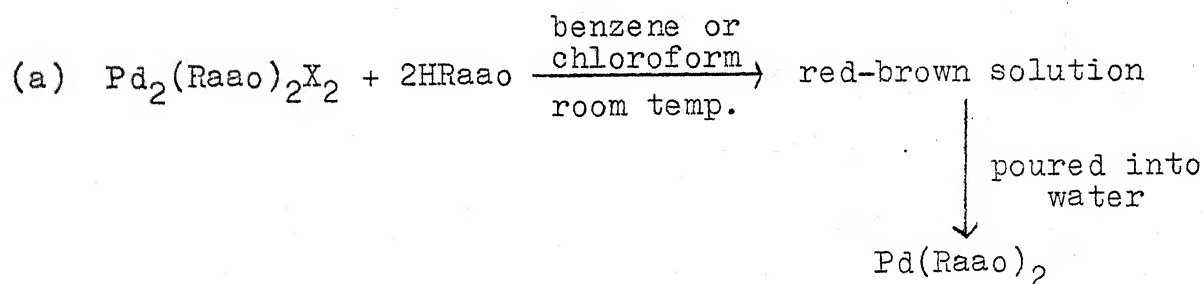
$$Pd(Raao)_2$$

    The conversion of $Pd(Raao)_2$ to $Pd_2(Raao)_2X_2$ have been achieved by

(c) the 1:1 reaction between $Pd(Raao)_2$ and $Pd(PhCN)_2X_2$
    in benzene or ethanol at room temperature

and (d) the 1:1 reaction between $Pd(Raao)_2$ and PdX_2 in

       boiling ethanol.

Reaction (a) and (b) have also been utilised in
synthesising mixed species of the type Pd(Raao)(R'aao) and
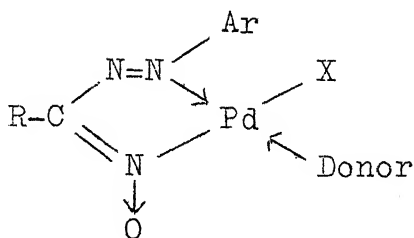Pd(azbz)(Raao) starting from suitable halo-bridged complexes
and HRaao.

The N-O stretching vibration in the infrared spectra of
palladium(II) arylazooximates appears in the range 1220-1280 cm^{-1}.
The high energy shift implies a five-membered chelate ring with
nitrone structure **5**. The moiety **5** gives rise to an intense band

5
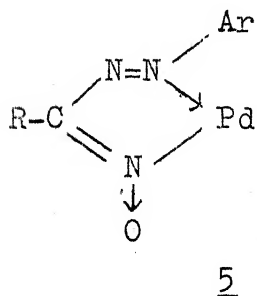
around $\sim$ 500 nm with extinction coefficient of 5000 per Pd
atom which probably arises from a $M \longrightarrow L$ charge transfer. The
bis-complexes exhibit a strong band with double-humped structure
at $\sim$ 600 nm ($\epsilon \sim$ 6000). The pmr spectra of $Pd(Meaao)_2$ and
Pd(azbz)(Meaao) show sharp and single resonance for the methyl
group at δ = 2.13 and 2.4 ppm respectively.

In Chapter III, the bridge-splitting reactions of
$Pd_2(Raao)_2X_2$ with different monodentate and bidentate Lewis
bases have been described. The known bridge-splitting reactions

of the halo-bridged complexes of palladium and platinum have
been summerised at the beginning. Monodentate amines and
triphenylarsine cleave the halogen bridge in $Pd_2(Raao)_2X_2$ to
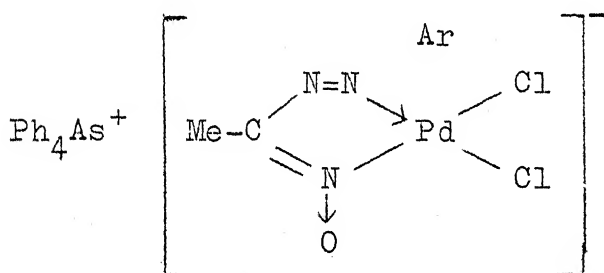yield products of the type 6.

$$R-C \begin{array}{c} N=N \\ \diagdown \\ N \end{array} \begin{array}{c} Ar \\ \diagup \\ Pd \diagup X \\ \diagdown Donor \end{array}$$
$$\downarrow$$
$$O$$

6

Since the bridge-splitting reaction is quite fast
with bulky bases like 2,6-lutidine and triphenylarsine, the
entering ligand is expected to occupy the position trans- to
the azo-end of Raao fragment (i.e. structure 6). When heated
around 200°C, the $\left[(Raao)Pd(am)X\right]$ complexes where R = aryl
and am = py, γ-picoline or aniline, lose am to produce the
halo-bridged species. The bridge-split products invariably
exhibit the intense band around 500 nm (characteristic of the
moiety 5). In $\left[(Raao)Pd(Donor)X\right]$ complexes, ν_{N-O} and ν_{Pd-Cl}
appear in the range 1240–1300 cm^{-1} and at $\sim$ 350 cm^{-1} respectively.
In the pmr spectra of these complexes, the methyl signal of
the arylazooximato (aao) fragment appears at $\delta \sim$ 2.3 ppm.

Bridge-splitting of $Pd_2(Raao)_2Cl_2$ by bidentate amines
like phen and en produces ionic complexes (7) which are 1:1
electrolytes in methanol and nitromethane. When treated with
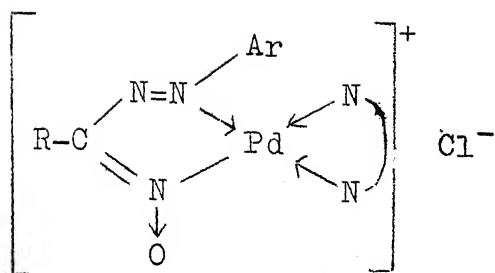
7

NaClO$_4$ in methanol, the complexes 7 are converted to the corres-
ponding perchlorates. Reaction of Ph$_4$As$^+$Cl$^-$ with Pd$_2$(Meaao)$_2$Cl$_2$
also leads to the formation of ionic product viz 8 which is an

8

1:1 electrolyte in acetonitrile and exhibits cis ν_{Pd-Cl} at
330 and 300 cm^{-1}.

With two equivalents of triarylphosphines (PAr$_3$),
Pd$_2$(Raao)$_2$X$_2$ gives rise to bridge-split products of the type 6.
On further addition of PAr$_3$, the aao chelate ring is opened at
the azo-end and in solution the following equilibrium exists:

.... (1)
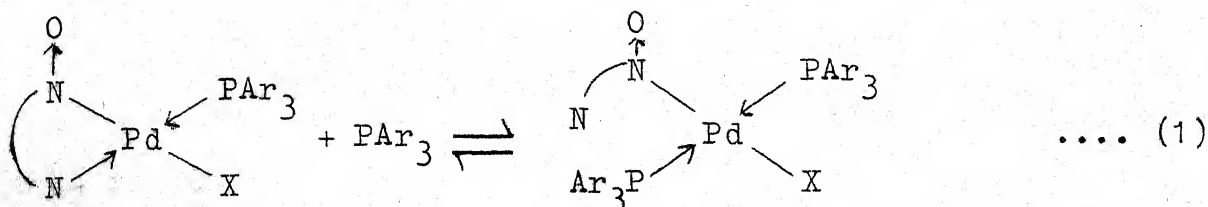
9

Monoamines and triphenylarsine, however, cannot bring about any further reaction beyond the bridge-splitting step. Triarylphosphines have been found to displace coordinated am's from $[(Meaao)Pd(am)X]$ complexes to yield $[(Meaao)Pd(PAr_3)X]$. Amines on the other hand can neither displace coordinated PAr_3 nor can open the aao chelate ring. An interesting synthesis of the $[(Raao)Pd(EAr_3)Cl]$ complexes where $E = P$ or As involves just mixing of stoichiometric amounts of $Pd(Raao)_2$ and trans-$[(EAr_3)_2PdCl_2]$ in benzene or chloroform.

Chapter IV concerns the ring-opening reactions of $Pd_2(Raao)_2X_2$. Complexes of the type $[(Meaao)Pd(PAr_3)_2X]$ have been isolated from concentrated solutions containing $Pd_2(Raao)_2X_2$ and PAr_3 (molar ratio 1:4). In $[(Meaao)Pd(PAr_3)_2X]$, the azo-end of the aao chelate ring is open. This opening of the azo-end is characterised by (i) the disappearance of ~ 500 nm band in the electronic spectrum and (ii) the appearance of new infrared absorption around 1490 cm^{-1}. The infrared spectra of $[(Meaao)Pd(PAr_3)_2X]$ suggest that the two PAr_3 molecules are trans- to each other (structure 9). In $[(Meaao)Pd(PPh_3)_2Cl]$, ν_{Pd-Cl} appears at 335 cm^{-1}; this indicates that the Cl atom possibly occupies the position trans- to the oximato end of the aao fragment.

In the room temperature pmr spectra of $[(Meaao)Pd(PAr_3)_2X]$ complexes, the methyl signal appears at an abnormally high-field region ($\delta = 0.87$ ppm). The high-field shift has been suggested to arise from the anisotropic diamagnetic shielding

of the methyl group by the phenyl rings of the phosphines.

In solution $\left[(Meaao)Pd(PAr_3)_2X\right]$ (X = Cl, Br) lose PAr_3 and a dynamic equilibrium (1) is established. The constants for the equilibrium (1) with different arylphosphines have been determined using the intensity of the $\sim$ 500 nm band as an index of the concentration of the closed-ring species. The observed values of the equilibrium constants parallel the basicities expected from cone angle considerations. Both tri-o-tolylphosphine and triphenylarsine have been found to be unable in opening the aao chelate ring. The inabilities possibly arise from excessive steric crowding on the bonding face of the P atom and the inherent weak basicity of the As center respectively. $Ph_2PCH_2CH_2PPh_2$ (Diphos, P-P) and $Ph_2PCH_2CH_2AsPh_2$ (arphos, P-As) react with $Pd_2(Meaao)_2X_2$ (molar ratio 2:1) in benzene to produce $\left[(Meaao)Pd\left(P\text{-}P(As)\right)X\right]$ where the aao fragment is open at the azo-end. The complexes exhibit no band around $\sim$ 500 nm in their electronic spectra. This together with the appearance of strong absorption around 1490 cm^{-1} in the infrared spectra suggest structure 10 for these complexes. The methyl
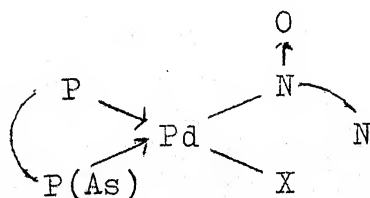

10

signal of the aao fragment (open at the azo-end) appears at δ = 1.80 ppm which shows that the methyl group is not much

shielded by the phenyl rings of the less flexible (chelated) phosphine. With one equivalent of diphos (or arphos), $Pd_2(Meaao)_2X_2$ (X = Cl, Br) give rise to $Pd(Meaao)_2$ and $(diphos)PdX_2$ (or $(arphos)PdX_2$). With $Pd_2(Meaao)_2X_2$, $[(Meaao)Pd(P-P(As))X]$ complexes (molar ratio 1:2) also yield $Pd(Meaao)_2$ and $(diphos)PdX_2$ (or $(arphos)PdX_2$).

Introduction of HCl gas into solution of $Pd_2(Raao)_2Cl_2$ in benzene opens the oxime-ends of the aao chelate rings with concomitant protonation of the oxime groups. The $Pd_2(HRaao)_2Cl_4$ complexes (structure 11) are quite unstable and readily eliminate
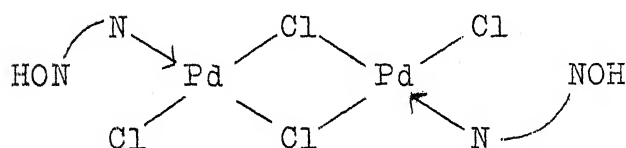
11

HCl in contact with bases (including moisture) to produce $Pd_2(Raao)_2Cl_2$. Structure 11 has been tentatively proposed for the $Pd_2(HRaao)_2Cl_4$ complexes since the complexes (i) exhibit strong and broad ν_{O-H} (~ 3100 cm^{-1}) and $\nu_{Pd-Cl(terminal)}$ (~ 350 cm^{-1}) in infrared spectra (ii) exhibit no band around 500 nm in electronic spectra and (iii) deposit yellow crystals of trans-$[(PPh_3)_2PdCl_2]$ on addition of PPh_3 to benzene solution of 11 Passage of HCl gas through benzene solution of $[(Meaao)Pd(PPh_3)_2Cl]$ also produces trans-$[(PPh_3)_2PdCl_2]$. Thus the aao chelate ring can be opened at either end depending on the attacking reagent. When both reagents (PAr_3 and HCl) are used successively in any

order, the entire ligand is eliminated with the formation of
trans- $\left[(PAr_3)_2PdCl_2\right]$.

The ring-opening and oxidative reactions of the bis-
complexes $Pd(Raao)_2$ constitute the subject matter of Chapter V.
Amines like py, aniline and γ-picoline open one aao chelate
ring in $Pd(Raao)_2$ to generate species of the type 12 in
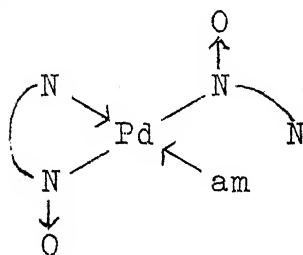
12

solution.   These species give rise to an intense electronic
band at $\sim$ 500 nm with extinction coefficient of $\sim$ 7000.   All
attempts to isolate the complexes 12 in crystalline state
however, failed.   The first isolable species of the type 12
was obtained with PPh_3.   With one equivalent of PPh_3, $Pd(Meaao)_2$
yields 13 which shows an intense band at 500 nm (ϵ = 7000) in
benzene .   The infrared spectrum of 13 exhibit absorptions
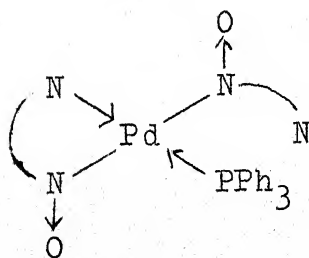
13

characteristic of both open and closed aao chelate rings.   In
room temperature pmr spectrum of $\left[(Meaao)_2Pd(PPh_3)\right]$, one broad

methyl signal at δ = 1.82 ppm is observed. The broadening of the methyl signal probably arises from fast exchange between open and closed aao ring. When a solution containing Pd(Meaao)$_2$ and PPh$_3$ in the molar ratio 1:2 in benzene is concentrated to a small volume, $\left[(\text{Meaao})_2\text{Pd(PPh}_3)_2\right]$ crystallises out as an orange solid. Since in the solid state the compound does not show any electronic band around 500 nm and its infrared spectrum in KBr exhibits only the characteristic absorptions of open aao fragment, structure 14 has been suggested for $\left[(\text{Meaao})_2\text{Pd(PPh}_3)_2\right]$. In
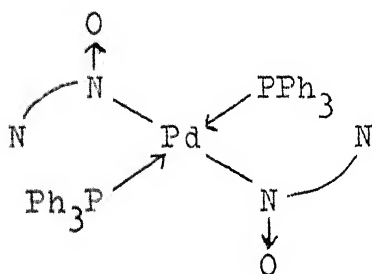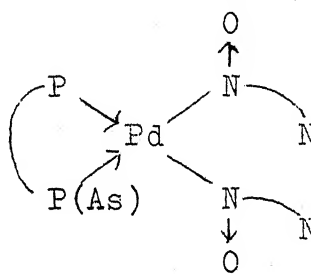
14   15

solution however, 14 is completely dissociated into 13 and PPh$_3$ (electronic and pmr data). With Pd(Meaao)$_2$, both tri-m-tolylphosphine and tri-p-tolylphosphine yield complexes of the type 13 whereas tri-o-tolylphosphine and triphenylarsine are unable to open the aao chelate rings in Pd(Meaao)$_2$. Complexes with both aao chelate rings open (at the azo-end) are obtained in the 1:1 reaction between Pd(Meaao)$_2$ and diphos (or arphos). The complexes $\left[(\text{Meaao})_2\text{Pd(diphos)}\right]$ and $\left[(\text{Meaao})_2\text{Pd(arphos)}\right]$ (15) exhibit no electronic band around 500 nm both in solid state and in solution. The infrared spectra confirm that both the aao rings are open at the azo-end. The pmr spectrum of

$\left[(Meaao)_2Pd(diphos)\right]$ exhibits a sharp methyl signal at $\delta = 1.80$ ppm which is characteristic methyl signal of the aao fragment (open at azo-end) in complexes containing bidentate phosphines. The mixed species Pd(Meaao)(azbz) reacts with one mol of PPh_3 to produce $\left[(Meaao)Pd(azbz)(PPh_3)\right]$. Both the infrared spectrum and the chemical shift of the methyl group (1.33 ppm) indicate that the aao chelate ring is opened at the azo-end by the entering PPh_3 molecule.

Introduction of HCl gas into solutions of $Pd(Raao)_2$ in benzene brings about the formation of $\underline{11}$ with simultaneous rejection of one mol of HRaao per Pd atom. If the reaction mixture is poured into water and stirred, the bis-complexes are regenerated. The complexes $\underline{11}$ can be isolated by adding hexane to the reaction mixture.

The oxidative addition of two mols of HMeaao to one mol of $\left[Pd(PPh_3)_4\right]$ in dehydrated ethanol leads to the formation of $\left[(Meaao)_2Pd(PPh_3)_2\right]$. Oxidation of $Pd(Raao)_2$ with dichlorine and dibromine in benzene (or chloroform) produces deep red solutions. These red solutions are believed to contain unstable Pd(IV) species in analogy with complexes of the type $\left[(Raao)_2Pt^{IV}X_2\right]$ which have been isolated from similar red solutions produced in the reaction between $Pt(Raao)_2$ and halogens. Excess halogens bring about complicated reaction leading to deposition of PdX_2 and unidentified organic products When the red solutions are heated or ethanol is added to them, $Pd_2(Raao)_2X_2$ complexes are precipitated.

In Chapter VI a brief report of the preliminary
investigation on the chemistry of arylazooximates of platinum
is presented. The synthetic procedures which yield $Pd_2(Raao)_2X_2$
are not applicable for the synthesis of $Pt_2(Raao)_2X_2$. Only
one halo-bridged arylazooximate namely $Pt_2(Meaao)_2Cl_2$ has been
synthesised by boiling $PtCl_2$ with HMeaao in dehydrated ethanol
for 48 hrs. The spectral characteristics of $Pt_2(Meaao)_2Cl_2$
(ν_{N-O}= 1290 cm^{-1}; ϵ_{550} = 5000 per Pt atom) are quite similar
to those of $Pd_2(Meaao)_2Cl_2$ and hence the structure of the
complex is believed to be similar to $\underline{3}$. $Pt_2(Meaao)_2Cl_2$
undergoes facile bridge-splitting reactions with amines like
py and aniline to give $\left[(Meaao)Pt(am)Cl\right]$ complexes which are
very much similar to the corresponding palladium species. On
stirring a mixture of K_2PtCl_4 and HRaao (R = Me, Ph) in aqueous
ethanol for 48 hrs, a dark solid is obtained. Addition of
ethanol to solution of the dark solid in chloroform deposits
dark crystals of the bis-complex $Pt(Raao)_2$. The bis-complexes
exhibit intense electronic band in unusually low energy region
($\sim$ 1080 nm). $Pt(Meaao)_2$ gives rise to well-defined epr signal
though bulk magnetic susceptibility measurement shows it to be
diamagnetic. Most possibly the epr signal arises from some
paramagnetic species present in small concentration. With
two equivalents of PPh_3, $Pt(Meaao)_2$ produces $\left[(Meaao)_2Pt(PPh_3)_2\right]$
(analogous to $\underline{14}$) which dissociates into $\left[(Meaao)_2Pt(PPh_3)\right]$ and
PPh_3 in benzene solution. The 1:1 reaction between $Pt(Meaao)_2$
and diphos in benzene results in the formation of
$\left[(Meaao)_2Pt(diphos)\right]$ (analogous to $\underline{15}$). The methyl signal of

the aao fragment in open-azo configuration exhibits high-field shift in both $[(Meaao)_2Pt(PPh_3)_2]$ and $[(Meaao)_2Pt(diphos)]$.

The oxidative addition of two mols of HMeaao to $[Pt(PPh_3)_4]$ in dehydrated ethanol yields $[(Meaao)_2Pt(PPh_3)_2]$. Oxidation of $Pt(Meaao)_2$ by dichlorine and dibromine in benzene produces deep red solutions from which complexes of the type $[(Meaao)_2PtX_2]$ have been isolated. These diamagnetic complexes exhibit one strong Pt-X stretching vibration and are expected to have a trans- configuration. Passage of HCl gas through solution of $[(Meaao)_2Pt(PPh_3)_2]$ in benzene leads to the formation of trans- $[(PPh_3)_2PtCl_2]$. $Pt(Meaao)_2$, on successive reaction with HCl and PPh$_3$ (in any order) produces trans- $[(PPh_3)_2PtCl_2]$. These reactions demonstrate that HCl opens the aao chelate ring at the oxime-end in platinum complexes also. Further studies on the arylazooximes of platinum are in progress.

VITAE

Born on December 1st, 1953 at Alowar (Rajasthan) the author had his early education at Pune, Jamshedpur and Burdwan. He passed the Higher Secondary Examination from Burdwan Raj Collegiate School, Burdwan in 1968. After obtaining his B.Sc.(Honours) and M.Sc. degrees in 1971 and 1973 respectively from Burdwan University, Burdwan, he joined the Ph.D. programme in Chemistry at the Indian Institute of Technology, Kanpur in July 1975.